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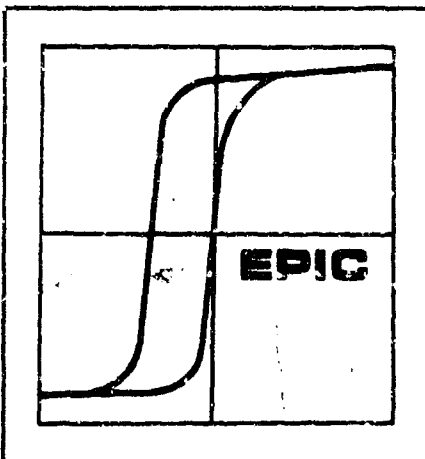
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PROJECT 72911 TASK 786.05

AD814147

# LEAD OXIDE

M. NEUBERGER

DATA SHEET DS-155  
MAY 1967



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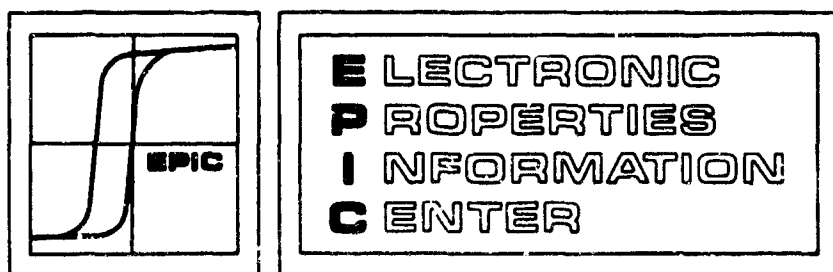
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# LEAD OXIDE

M. NEUBERGER

DATA SHEET DS-155

MAY 1967

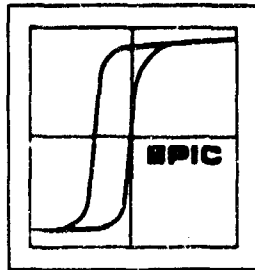


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## FOREWORD

This report was prepared by Hughes Aircraft Company, Culver City, California, under Contract Number AF 33(615)-2460. The contract was initiated under Project No. 7381, "Materials Application," Task No. 738103, Materials Information Development, Collection, and Processing." The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Mr. R. F. Klinger, Project Engineer.

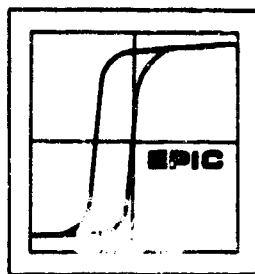
The Electronic Properties Information Center conducts documentary research based on the collection, analysis, and review of the scientific and technical literature relevant to the electrical, electronic, and magnetic properties of materials. The primary objective of this program of evaluation and correlation is to provide a source of competent information to the DoD community. By means of several series of publications such as Data Sheets, Special Reports, Interim Reports and several services such as Computer Bibliographies, technical questions answering services, and special studies, research and development support is made available to this extended community.

The initial step in the preparation of this data sheet was retrieval, by means of a modified coordinate index, of all lead oxide literature in the EPIC file which comprised 37 accessions and all these are listed in the Reference Section. Bibliographies were also reviewed to ensure the inclusion of all relevant literature.

If data available from several sources are judged to be equally valid, then all are given. Data are considered questionable and rejected for inclusion because of faulty or dubious measurements, unknown sample composition, or if more reliable and inclusive data are available from another source. Selection of data is based upon evaluation of that which is most representative, precise, reliable and inclusive over a wide range of parameters.

Within every property section we have tried to include every available parameter and range of experimental condition found in the literature. Measurement environment and sample specification are included when available. Some alterations in units and presentation may be made to facilitate comparison with other experimental data.

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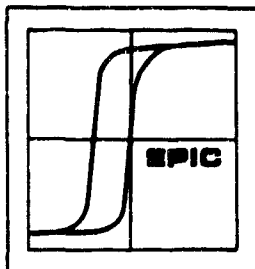
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This report consists of the compiled data sheets on lead oxide. A full list of EPIC publications to-date appears at the end of the report.

The author wished to acknowledge the assistance afforded by Dr. J. J. Grossman in reviewing the experimental data, and the contribution of Dr. Sheldon Welles in the review of the compilation.

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### ABSTRACT

These data sheets present a compilation of a wide range of electronic properties for lead oxide. Electrical properties include conductivity, resistivity and dielectric constant. A wide variety of photoelectronic phenomena is shown. Energy data include energy bands, energy gap, and energy levels, as well as effective mass tables, phonon energy dispersion and work function. The optical properties include absorption, reflection, and refractive index. Data on several physical phenomena, such as thermal conductivity, Debye temperature, magnetic susceptibility and Richardson's Constant are presented. Thermoelectric data is given. Each property is compiled over the widest possible range of parameters including bulk and film form, from references obtained in a thorough literature search.

A summary of crystal structure and phase transitions has been included.

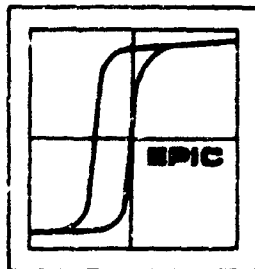
This report has been reviewed and is approved for publication.

*Sheldon J. Welles*

Dr. Sheldon Welles, Head  
Electronic Properties Information Center

*John W. Atwood*

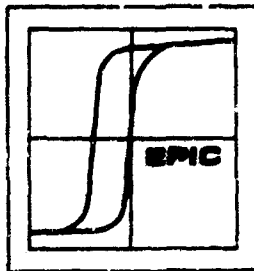
John W. Atwood  
Project Manager



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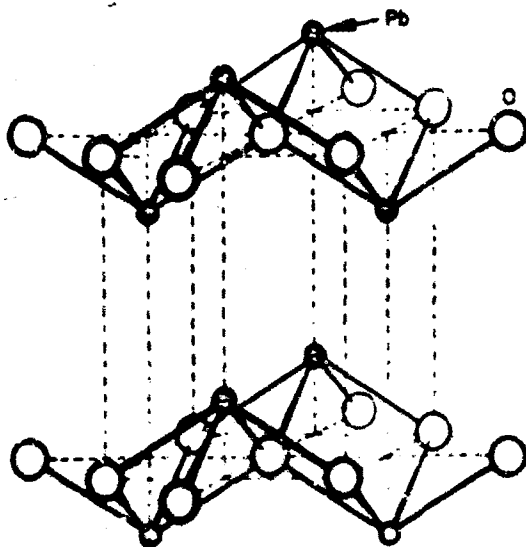


## INTRODUCTION

Lead forms a series of interconvertible oxides, extremely sensitive to changes in temperature and oxidation during preparation. The table of lattice constants on page 4 is some indication of the complexity of the problem.

In general, the lead monoxide is most commonly obtained by oxidation of lead. It exists in two polymorphic forms:

### RED-TETRAGONAL



Crystal structure of Tetragonal  $\text{PbO}^{(1)}$

Litharge is the alpha-lead monoxide. It is red tetragonal, and artificial crystals are tabular on (001)

Mohs Hardness = 2

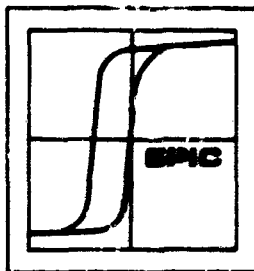
Density = 9.14

Index of refraction is:

$$n_L = 2.665$$

$$n_{Li} = 2.535$$

and dispersion is very high, (8.8)<sup>(2)</sup>



## YELLOW ORTHORHOMBIC

At 530°C Litharge converts to Massicot, the beta-lead oxide. This is yellow orthorhombic and artificial crystals are tabular on (100) and may be twinned.

Mohs Hardness = 2

Density = 9.56

### Index of refraction

Axis	$n_{Li}$	Absorption
x	2.51	
y	2.61	light yellow
z	2.71	deep yellow

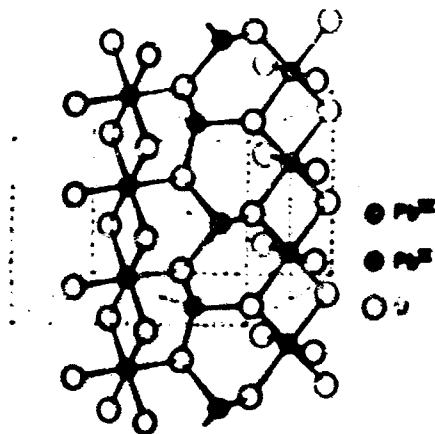
Minium, the tetroxide  $Pb_3O_4$  is red lead and is tetragonal.

Mohs Hardness = 2-3

Density = 4.6

$n_{Li}$  = 2.42±0.02

(2)



Crystal structure of  $Pb_3O_4$

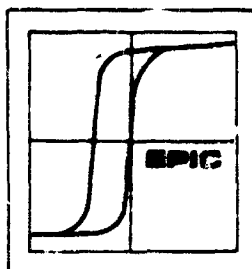
(1)

Plattnerite is the dioxide,  $PbO_2$ . It is black tetragonal.

Mohs Hardness = 5-5.5

Density = 8.5

(2)



## LATTICE CONSTANTS

### Red Tetragonal

Recent lattice constants from x-ray and neutron diffraction studies for the red tetragonal lead monoxide are:<sup>(3)</sup>

$$a_o = 3.9759\text{A} \quad 300^\circ\text{K}$$

$$c_o = 5.023\text{A}$$

Later data is:<sup>(4)</sup>

$$a_o = 3.96 \pm 0.01\text{A}$$

$$c_o = 5.01 \pm 0.01\text{A}$$

Each lead atom is bound to four oxygen atoms forming a square-based pyramid with a lead atom at the apex. Each oxygen atom is surrounded tetrahedrally by four lead atoms.

$$\text{Pb-O} = 2.30\text{A}$$

### Yellow Orthorhombic

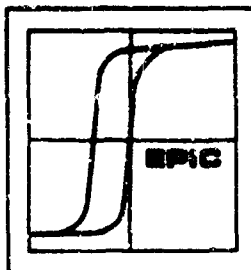
Leciejewicz has also studied the yellow orthorhombic lead monoxide<sup>(5)</sup> by neutron diffraction methods and obtains the same values as Byström<sup>(6)</sup>.

$$a_o = 5.476\text{A}$$

$$b_o = 5.876$$

$$c_o = 4.743$$

Each lead atom is bounded by oxygen atoms at a distance  $\text{Pb-O} = 2.21 \pm 0.02\text{A}$ . Oxygen and lead atoms lie on the same level forming a zigzag chain. Neighboring chains are located at a distance of  $2.49 \pm 0.02\text{A}$ . Lead atoms are  $\text{Pb-Pb} = 3.51 \pm 0.02\text{A}$  indicating weak interlayer bonding.

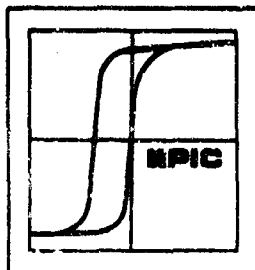


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Compound	Symmetry*	Lattice Constant (Å)				Remarks
		a <sub>o</sub>	b <sub>o</sub>	c <sub>o</sub>	β	
PbO	O	5.476	5.876	4.743		Yellow
	T	3.947		4.988		Red
	T	3.972		5.023		Red
PbO <sub>2</sub>	O	5.486	5.939	4.938		(001) Orientation
	T	4.731		3.367		Plattnerite
	T	4.955		3.383		PbO <sub>1.99</sub>
Pb <sub>2</sub> O <sub>3</sub>	M	7.050	5.616	3.865	99.9	
Pb <sub>3</sub> O <sub>4</sub>	T	8.788		6.551		Minium, natural crystal
	T	8.86		6.66		Minium, natural crystal
Pb <sub>5</sub> O <sub>8</sub>	T	5.508		5.40		
	M	22.92	10.81	7.72	91.3	PbO <sub>1.586</sub>
	O	5.444	5.948	4.977		PbO <sub>1.85-1.92</sub>
	O	7.66	7.80	5.50		β-PbO <sub>1.47-1.51</sub>
	O	7.655	7.793	5.496		PbO <sub>1.43</sub> , Pseudocubic
	O	7.667	7.753	5.458		PbO <sub>1.50</sub> , Pseudocubic
	O	7.805	7.805	5.471		PbO <sub>1.372-1.563</sub>
	C	5.44				PbO <sub>1.6-1.72</sub>
Pb <sub>2</sub> O	C	5.39				Unstable, decomposes into PbO+Pb

\*O Orthorhombic  
T Tetragonal  
M Monoclinic  
C Cubic

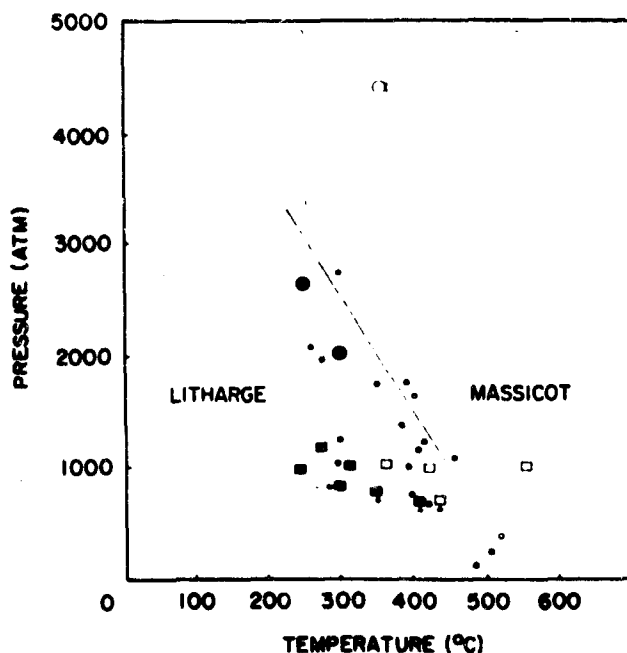
(7)



Under pressures up to 60,000 atmospheres and temperatures of 100°C to 600°C, several lead oxide polymorphs are produced.

PbO Litharge  $\rightleftharpoons$  Massicot

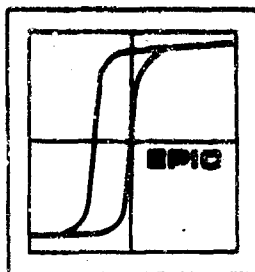
The equilibria data on this transition are equivocal; the yellow orthorhombic form is more stable at high temperatures and the transition ranges from 475° - 585°C. The high temperature Massicot has the higher density, and the next graph illustrates the complexity of the data.



Univariant pressure-temperature curve for the reaction litharge  $\rightleftharpoons$  massicot showing hydrothermal and uniaxial data.

<u>Symbols</u>	<u>Starting material</u>	<u>End Product</u>
○	Litharge/massicot mixture	Massicot
●	Litharge/massicot mixture	Litharge
□	Massicot	Massicot
■	Massicot	Litharge
↑	Heated dry to T; P then raised	
→	Raised P; then heated to T	
○	Runs with uniaxial device	

(Ref. 27813)



$PbO_2$  I (rutile-tetragonal)  $\rightleftharpoons$   $PbO_2$  II (orthorhombic)

The tetragonal form is stable at temperatures to  $600^\circ\text{C}$  at pressures below 12,000 atm. Above this pressure the orthorhombic form appears and is stable at  $20^\circ\text{C}$ . (Ref. 27813)

Closer study on the pure dioxide indicates that under atmospheric pressure, the tetragonal form was stable from  $20^\circ\text{C}$  to  $230^\circ\text{C}$ . The maximum rate of transition of the rhombic form was at  $100^\circ\text{C}$ . At  $20^\circ\text{C}$  and 30,000 kg/sq. cm., the tetragonal form changed to the rhombic. This paper suggests a third form of the dioxide close to the fluorite (b. c. c.) but it is more likely pseudocubic. (9)

$Pb_2O_3$  is formed and stable around  $500^\circ\text{C}$  to  $600^\circ\text{C}$  and above 15,000 atmospheres and then decomposes to  $Pb_3O_4$ . These are black vitreous crystals.

$Pb_3O_4$   $\rightleftharpoons$   $PbO + Pb_2O_3$  between  $100^\circ\text{C}$  and 35,000 atmospheres to  $400^\circ\text{C}$  and 10,000 atmospheres.

(Ref. 27813)

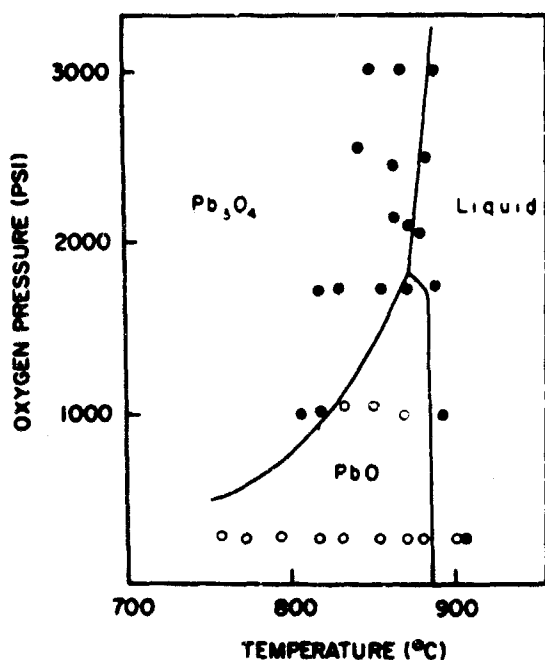
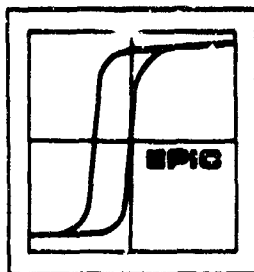
Between  $PbO_2$  and  $Pb_3O_4$  several oxides are formed by the decomposition of  $PbO_2$  in air. It has been suggested that two phases occur:  $Pb_{12}O_{19}$  and another compound  $Pb_{12}O_{17}$  which has a very narrow stability range in air. Another qualifying factor is the preparation method as  $PbO_2$  reduction yields better crystallinity than  $PbO$  oxidation. However, with increased oxygen pressure crystallinity improves in the  $PbO$  oxidation process.

(Ref. 14479)

$Pb_{12}O_{19}$

Reduction of  $PbO_2$  has yielded good samples of this monoclinic crystal.

$$\begin{aligned} a_o &= 5.496\text{A} \\ b_o &= 5.424 \\ c_o &= 5.392 \\ \beta &= 89^\circ 30' \end{aligned}$$

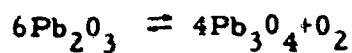
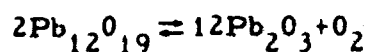
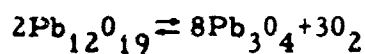
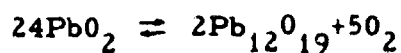


Phase diagram for  $\text{PbO} - \text{Pb}_3\text{O}_4$  -  
Liquid Eutectic

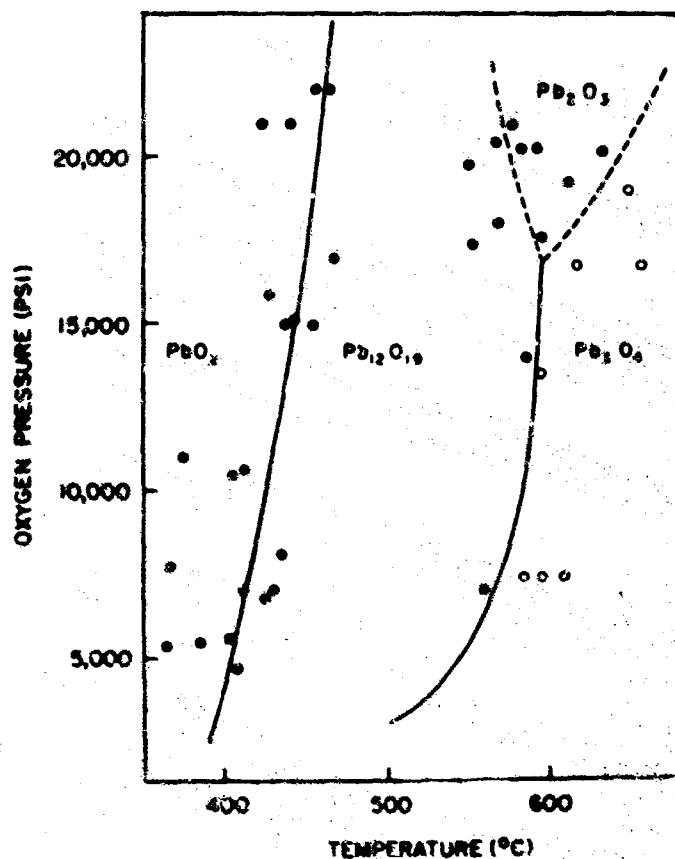
- $\text{Pb}_3\text{O}_4$
- $\text{PbO}$  (yellow)
- Liquid

(Ref. 14479)

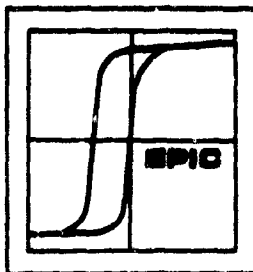
Temperature-pressure phase diagram  
at high oxygen pressures. Above  
1 kbar,  $\text{Pb}_2\text{O}_3$  is a stable phase.



- $\text{PbO}_2$
- $\text{Pb}_{12}\text{O}_{19}$
- $\text{Pb}_2\text{O}_3$
- $\text{Pb}_3\text{O}_4$



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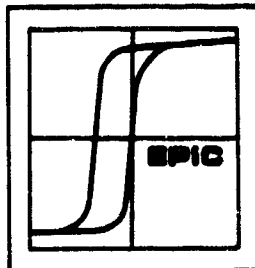
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Lead monoxide has a high refractive index and a high dispersion (8.8) which should make this material highly suitable for certain optical uses. Films of this material are adherent and fairly strong; they do not flake off easily.

(Ref. 4911)

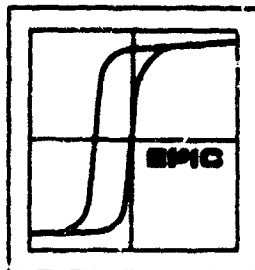
They may be vapor-deposited and under controlled conditions yields plates of the red tetragonal form  $2 \times 0.5 \mu$ , about  $0.005 \mu$  thick (50A). The plates are upright and markedly oriented to (110).<sup>(8)</sup>



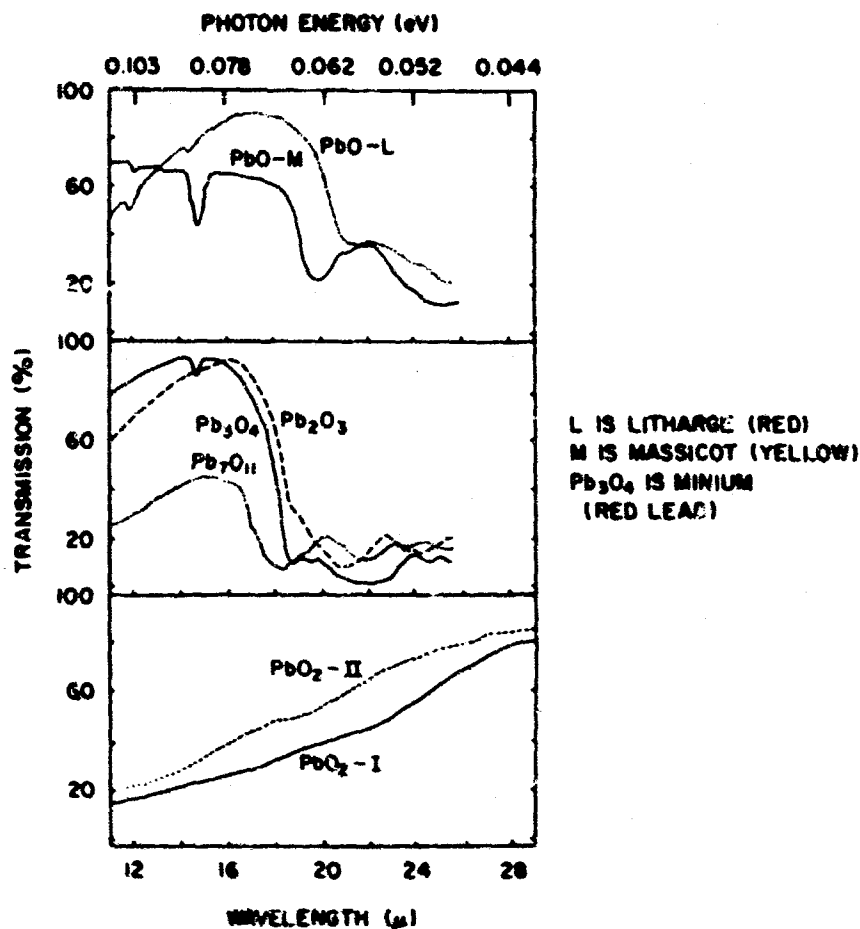


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**LEAD OXIDE  
ABSORPTION COEFFICIENT ( $\alpha$ )**



Transmission as a function of wavelength at 300°K, for several compounds in the lead oxide series:

L is litharge, the red tetragonal lead monoxide.

M is massicot, the yellow orthorhombic lead monoxide.

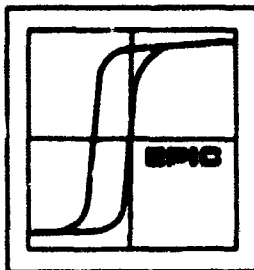
Pb<sub>2</sub>O<sub>3</sub> crystals are black and well-formed.

PbO<sub>2</sub> occurs in two forms, tetragonal "rutile" form and orthorhombic "a" form.

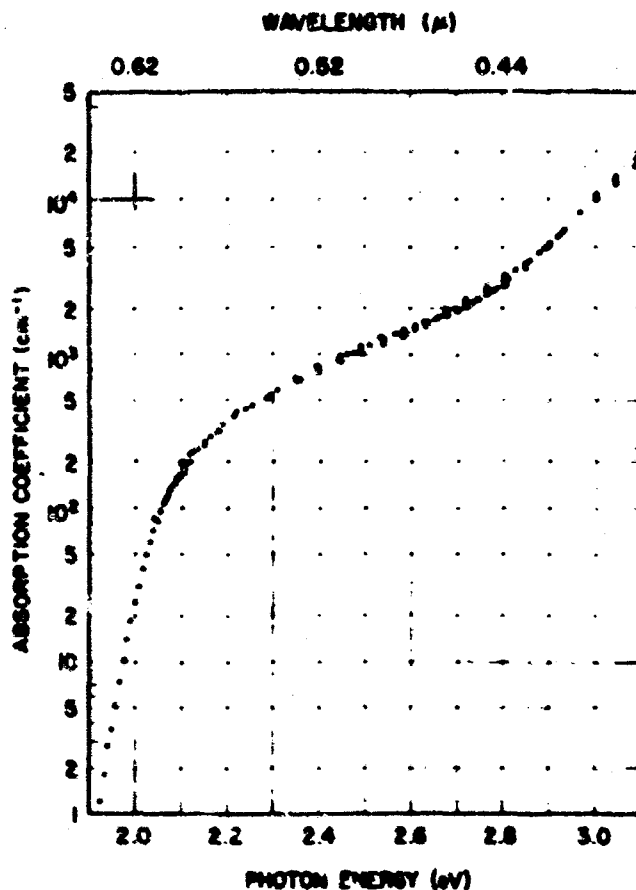
Pb<sub>3</sub>O<sub>4</sub> is minium, (bright scarlet "red lead") and forms in tetragonal single crystals.

Pb<sub>7</sub>O<sub>11</sub> has since been shown to be identical with Pb<sub>12</sub>O<sub>19</sub> (Ref. 14479).

(Ref. 27813)



**LEAD OXIDE**  
**ABSORPTION COEFFICIENT ( $\alpha$ )**

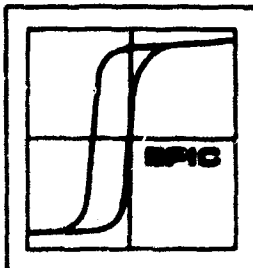


Absorption coefficient of tetragonal lead monoxide as a function of photon energy at 300°K. Single crystals were grown hydrothermally and the transparent red platelets were from 4 to 245  $\mu$  thick. Crystals were generally n-type,  $n = 10^{17} \text{ cm}^{-3}$  and (001) oriented. Illumination parallel to (001) from 6530Å to 4000Å.

The direct energy gap =  $2.84 \pm 0.03 \text{ eV}$

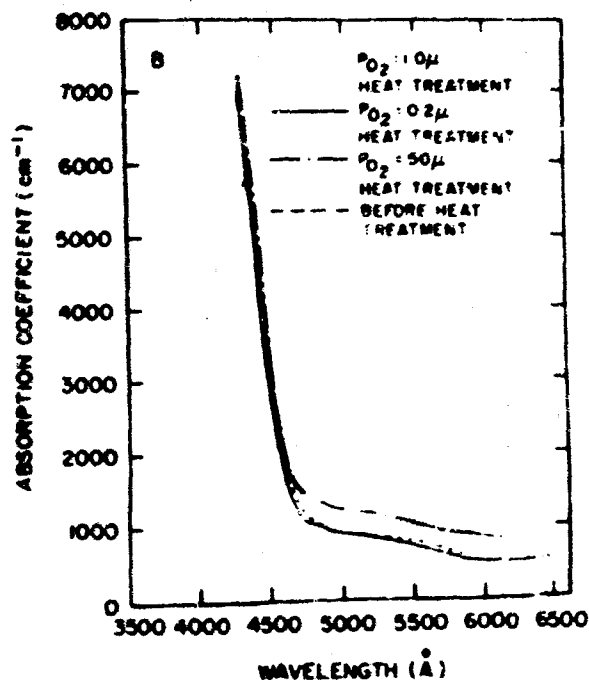
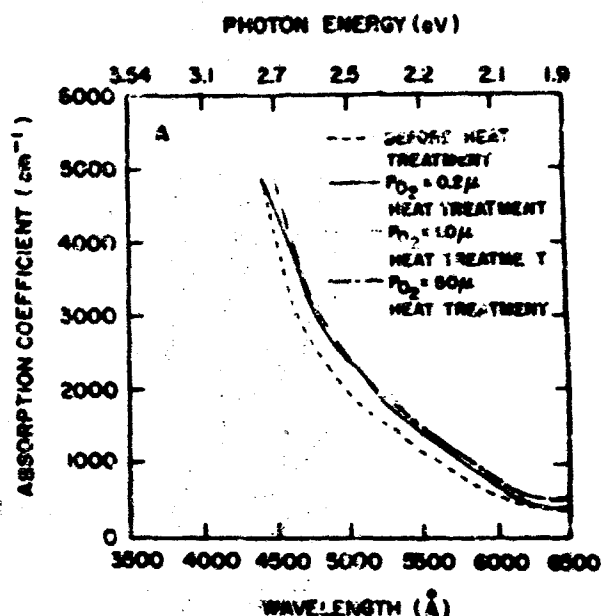
The indirect energy gap =  $1.936 \pm 0.01 \text{ eV}$

(Ref. 27801)



## LEAD OXIDE

### ABSORPTION COEFFICIENT ( $\alpha$ )

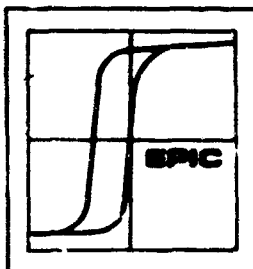


Absorption coefficient as a function of wavelength in vacuum-deposited polycrystalline lead monoxide films at 300°K. The substrates were kept at 120°C and the deposition was under reduced oxygen pressure. The as-deposited films were always tetragonal and n-type. When heated to the colour change from reddish brown to yellow, the crystal structure became orthorhombic. Transition temperatures vary with oxygen pressure.

- A Tetragonal films, 50 to 75 microns thick, n-type as deposited; p-type after heat treatment. Maximum resistivity is  $2 \times 10^{11}$  ohm cm. Absorption edge at 2.0 eV.
- B Orthorhombic films formed by heating from 350 to 400°C at low oxygen pressures. Change is from n- to p-type at 1 micron oxygen pressure and above. Maximum resistivity is  $1 \times 10^{13}$  ohm cm. Absorption edge at 2.6 eV.

Heat treatment at 300°C

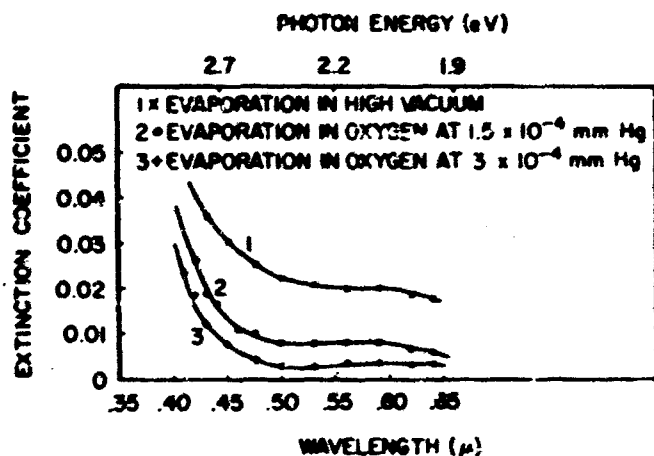
(Ref. 26041)



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## LEAD OXIDE

### ABSORPTION COEFFICIENT ( $\alpha$ )

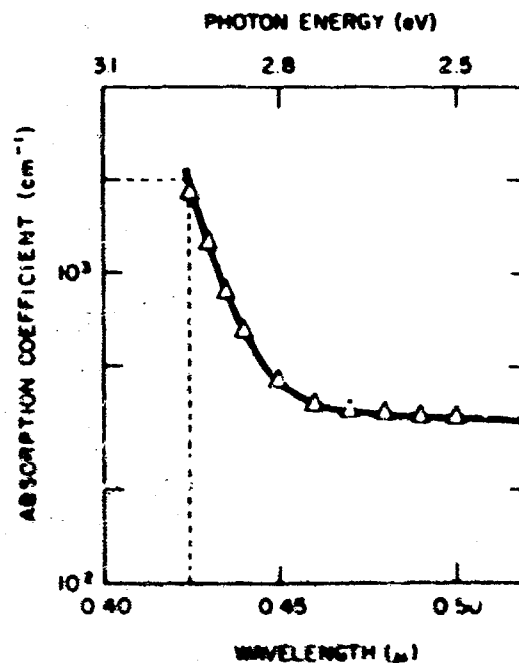


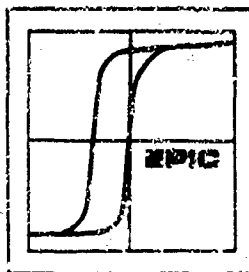
The extinction coefficient of a polycrystalline lead monoxide film at 300°K. The film is deposited at 300°C in either a high vacuum or in an oxygen atmosphere and has an orthorhombic crystal structure. Thickness ranges from 0.056 to 248 microns. Absorption is high in the ultraviolet in all cases, however, increase in oxygen pressure decreases the metallic lead and materially reduces the absorption.

(Ref. 4911)

Absorption coefficient as a function of wavelength at 300°K for single crystals of yellow lead oxide, about 10 microns thick. Absorption coefficient =  $2.0 \times 10^3$  cm<sup>-1</sup> at 0.42 microns.

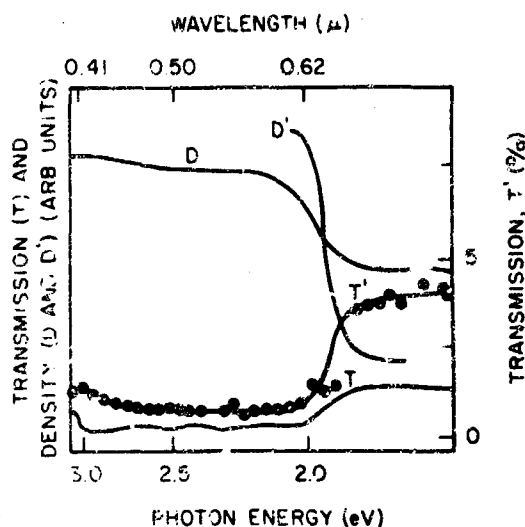
(Ref. 16327)





## LEAD OXIDE

### ABSORPTION COEFFICIENT ( $\alpha$ )



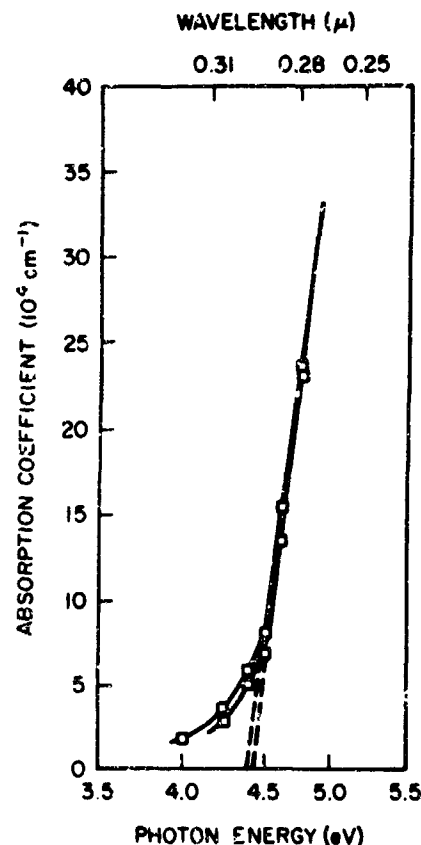
Optical density and transmission at 300°K as a function of wavelength in single crystal, red lead monoxide, tetragonal symmetry. These crystals were photoconductive with electrical resistivity of  $10^{10}$  to  $10^{12}$  ohm cm. The optical energy gap is determined at  $1.96 \pm 0.06$  eV.

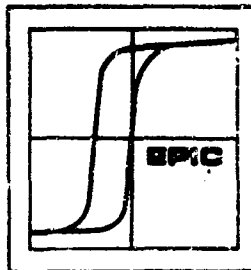
- D -- Density
- D' -- This curve is derived from data obtained by increasing the instrumental sensitivity.
- T -- Transmission
- T' -- Transmission data recorded on a second, more sensitive instrument.

All data is obtained from diffuse reflection spectra. (Ref. 16601)

Absorption coefficient as a function of wavelength for lead dioxide films at 300°K. The films are vacuum deposited from a powder and are polycrystalline. The optical energy gap is given as  $4.45 \pm 0.032$  eV.

(Ref. 3281)

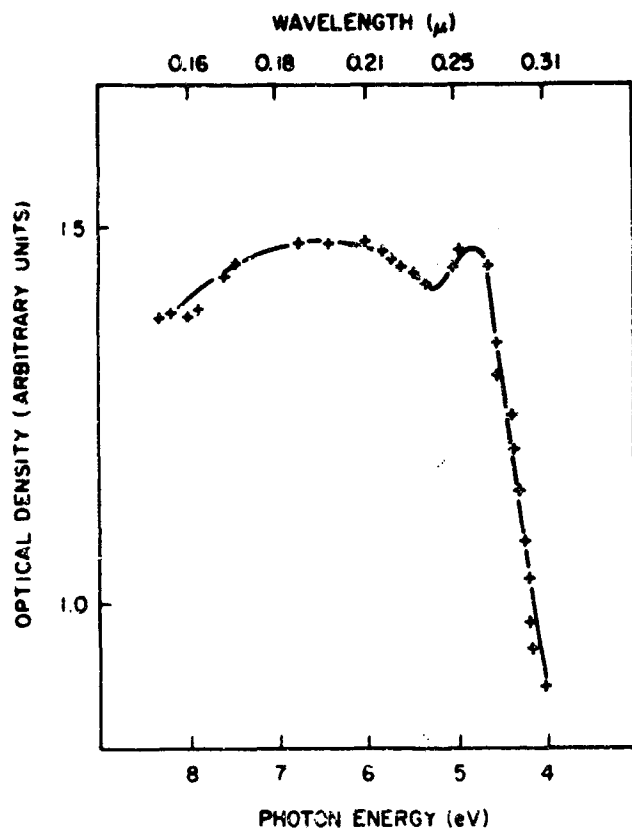




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## LEAD OXIDE

### ABSORPTION COEFFICIENT ( $\alpha$ )

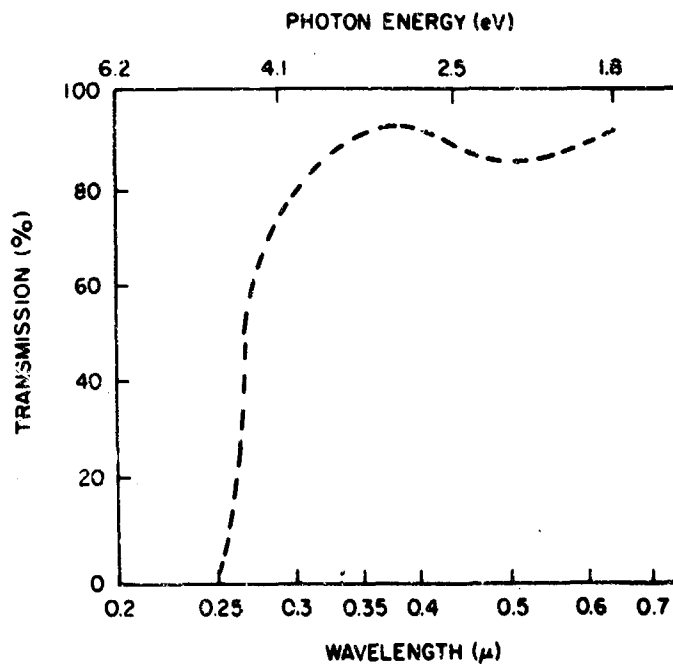


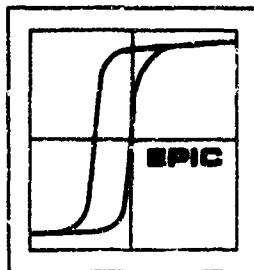
Optical density as a function of wavelength at 300°K in vacuum deposited lead film, heated in air at 650° C for 15 minutes. The optical edge at about 4.5 eV appears to agree with that for the dioxide as given in (3281) and it is possible that the heating in air has produced a mixture of the monoxide and the dioxide, although the author considers this the monoxide.

(Ref. 3418)

Transmission as a function of wavelength at 300°K for a lead dioxide film, vacuum deposited. The optical energy gap is given as  $4.45 \pm 0.032$  eV at 300°K.

(Ref. 3281)





**LEAD OXIDE**

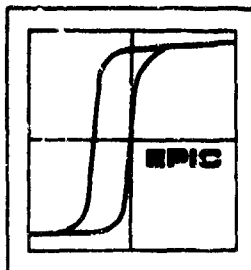
**DEBYE TEMPERATURE ( $\theta_D$ )**

$\theta_D$ ( $^{\circ}\text{K}$ )	Sample	Temp. Range ( $^{\circ}\text{K}$ )	Method of Measurement
145	Yellow PbO	51-250	Specific Heat
156	Red PbO	51-250	Specific Heat
79.4	Pb <sub>2</sub> O <sub>3</sub>	51-298	Specific Heat

E. G. King, Low Temperature Heat Capacities and Entropies at 298.15 $^{\circ}\text{K}$   
of Lead Sesquioxide and Red and Yellow Lead Monoxide

J. Amer. Chem. Soc. v 80,  
May 20/1958, pg 2400





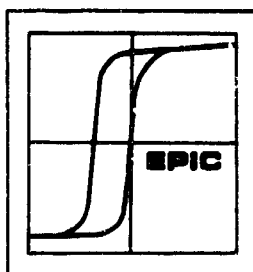
# LEAD OXIDE

## DIELECTRIC CONSTANT ( $\epsilon$ )

Symbol	Value	Sample	Method of Measurement	Temperature ( $^{\circ}$ K)	Ref.
$\epsilon_0$	25.9	PbO	at $10^8$ cps	298	*
	25.9	PbO	Calc. from ion polarizability (117.8 Å)	298	13715
		<u>Pressed powder discs</u>			
	35	yellow PbO sintered at $700^{\circ}$ C	100 c to 10 kc	300	14479
	15	Pb <sub>2</sub> O <sub>3</sub>	100 c to 10 kc	300	14479
	20	Pb <sub>3</sub> O <sub>4</sub>	100 c to 10 kc	300	14479
	32	red PbO	100 c to 10 kc	300	14479

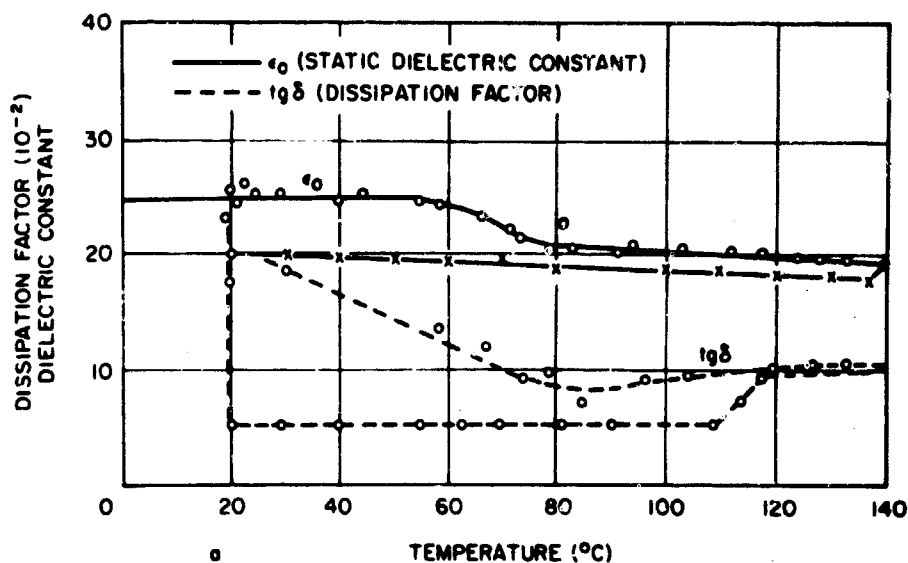
$\epsilon_0$  is the static dielectric constant and is only value obtained for the lead oxides.

\* Handbook of Physics and Chemistry, 47th Ed. pg E-56.

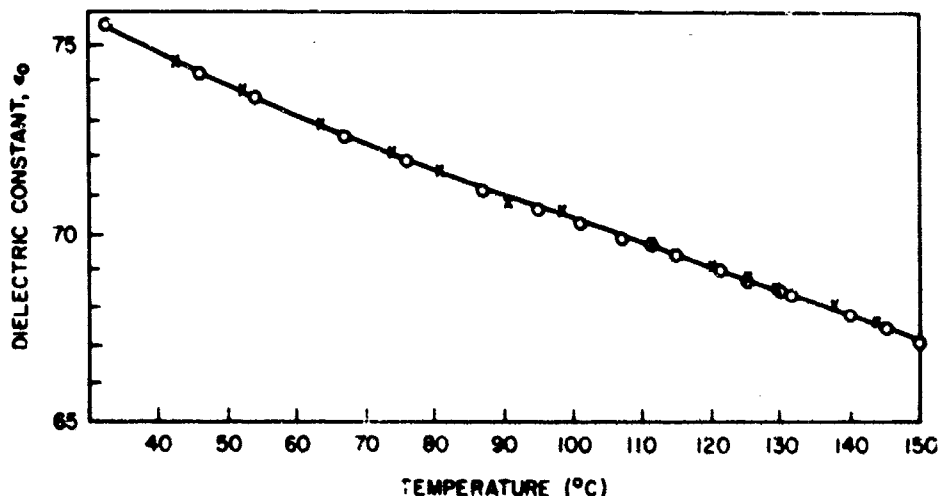


# LEAD OXIDE

## DIELECTRIC CONSTANT ( $\epsilon$ )



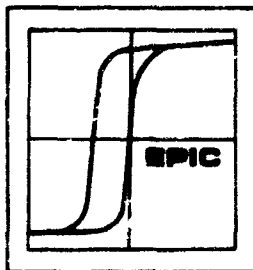
Dielectric constant and dissipation factor as a function of temperature. Both properties are hysteretic and require about 24 hours to return to the original value. This hysteresis is due not only to the heating but to a temporary structure change. Data taken at 1 kc.



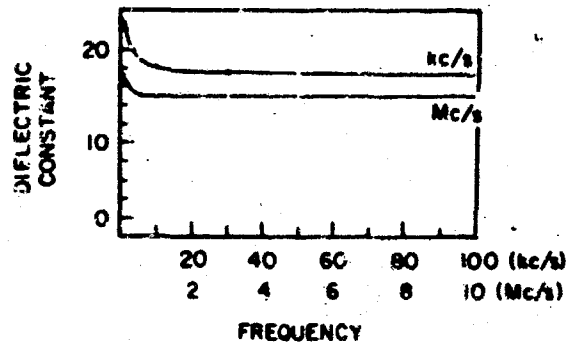
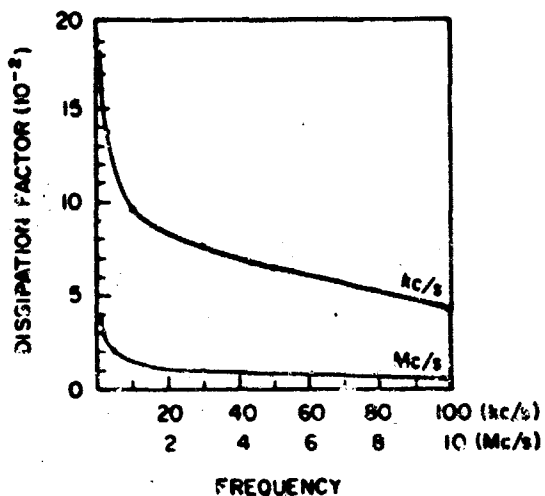
Dielectric constant as a function of temperature at 1 Mc

These data are taken on yellow lead monoxide in polycrystalline sintered pellets. The material is prepared by heating the red tetragonal form at 700°C for two hours. The yellow form is then stable at 20°C. Resistivity is about  $5 \times 10^7$  ohm cm.

(Ref. 8617)

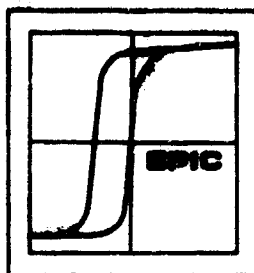


**LEAD OXIDE**  
**DIELECTRIC CONSTANT ( $\epsilon$ )**

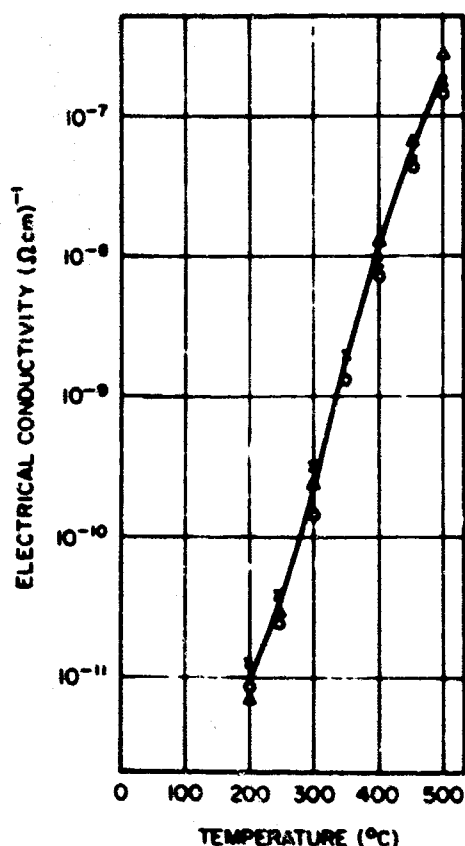


Curves of dielectric constant and dissipation factors for same material as on preceding page. Data is taken as a function of frequency at 20°C.

(Ref. 8617)

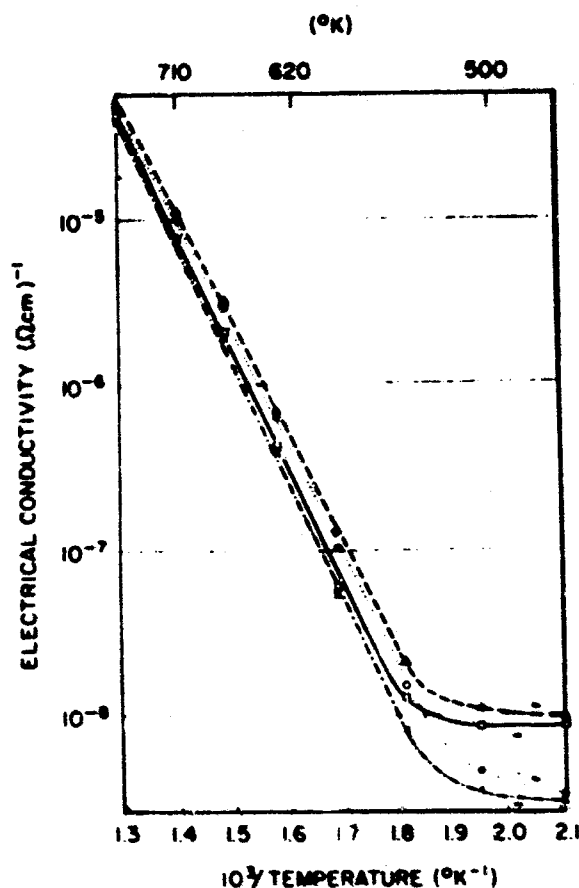


**LEAD OXIDE  
ELECTRICAL CONDUCTIVITY ( $\sigma$ )**



log Electrical conductivity as a function of temperature for pure lead monoxide in pressed powder pellets. These are annealed at 600°C at atmospheric pressure.

(Ref. 3936)

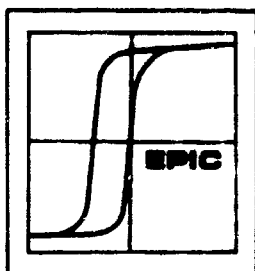


log Electrical conductivity as a function of reciprocal temperature for 2 samples of purified lead monoxide, yellow orthorhombic, in sintered pressed powders.

Sample I | □ increasing temperature  
          | Δ decreasing temperature

Sample II | x increasing temperature  
          | o decreasing temperature

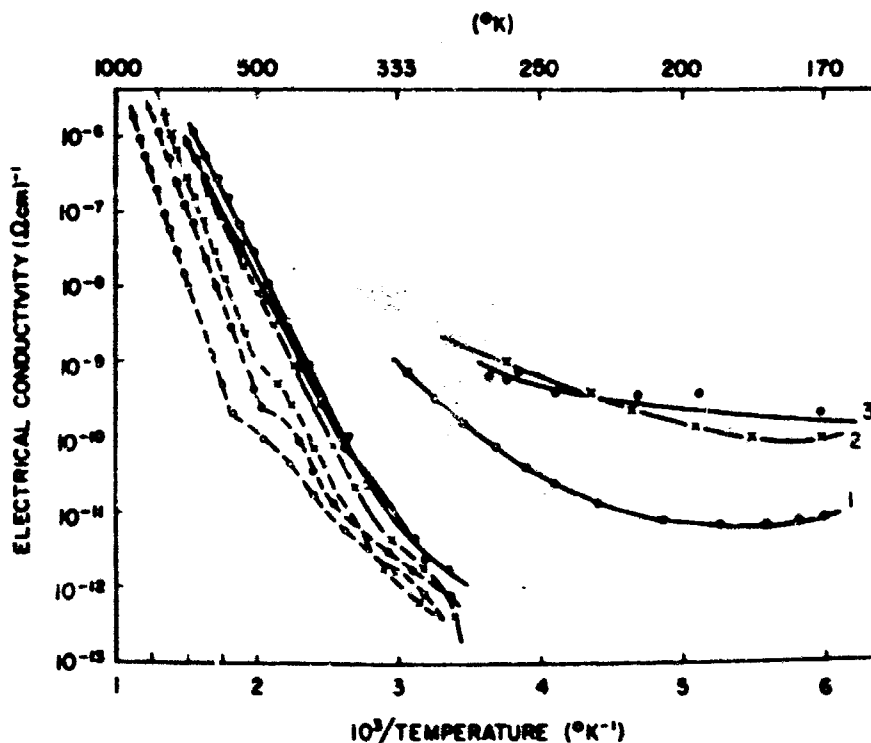
(Ref. 9490)



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## LEAD OXIDE

### ELECTRICAL CONDUCTIVITY ( $\sigma$ )

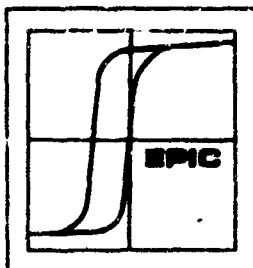


log Electrical conductivity as a function of reciprocal temperature in lead monoxide films, vacuum deposited. Layers were 1-3 microns thick with initial resistivity of  $10^9$  to  $10^{10}$  ohm cm. These layers were not photosensitive.

Heating in air at 723°K for 10 minutes changed colour from yellow to orange and raised the energy gap from about 1.5 eV to 2.0 eV. Heating in air, sulfur or selenium produced photosensitive layers. When heated in sulfur vapour, the film becomes sensitive in the visible because of the formation of lead sulfide which is sensitive in the infrared.

- Unheated
- - - Heated
- 1, 2— heated in sulfur vapour
- 3— heated in selenium vapour

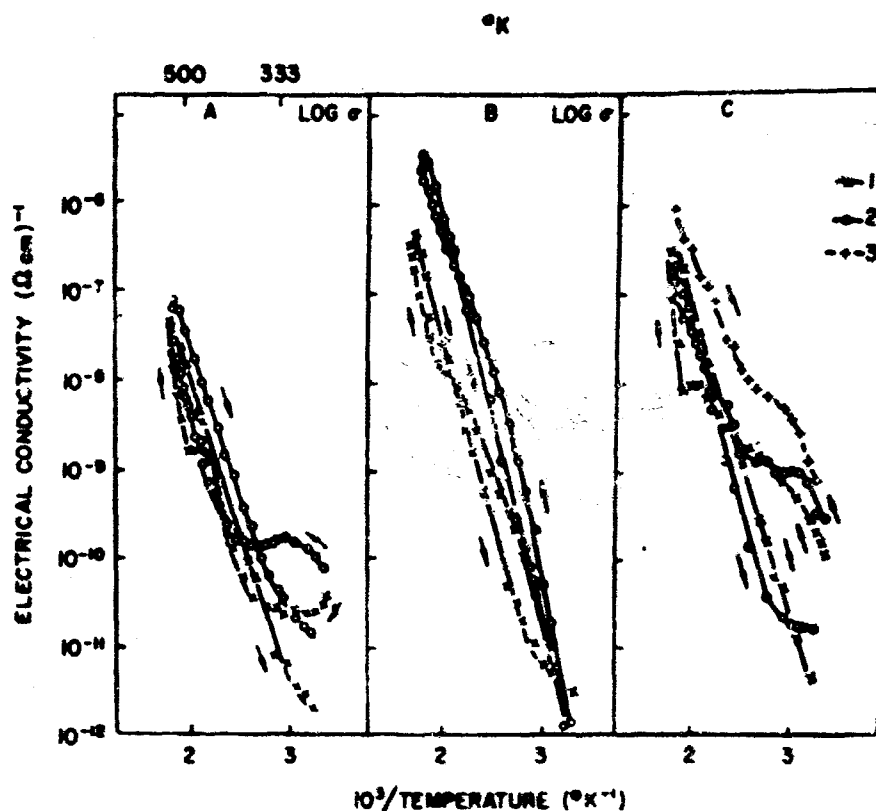
(Ref. 3551)



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# LEAD OXIDE

## ELECTRICAL CONDUCTIVITY ( $\sigma$ )



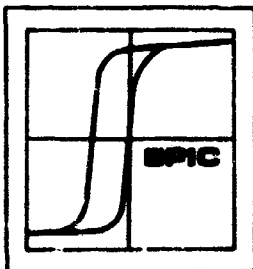
log Electrical conductivity as a function of reciprocal temperature in bulk and surface of polycrystalline, red, lead monoxide.

- 1 surface conductivity
- 2 volume conductivity
- 3 volume conductivity of a sample dried for 15 min. at 30-40°C

- a. non-activated samples
- b. activated by heating to 140°C
- c. activated samples kept in moist air for 10 days.

During heating, the loss of adsorbed moisture results in a decrease of conductivity in the surface layers. Heating also causes absorption of oxygen at first in the surface layers and then throughout the bulk. The hysteresis is connected with changes in the energy structure resulting from lattice ordering which starts at 215°C.

(Ref. 3415)

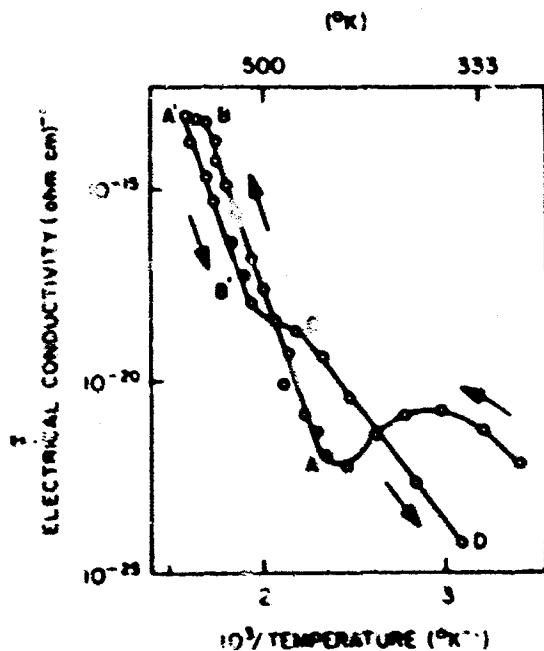
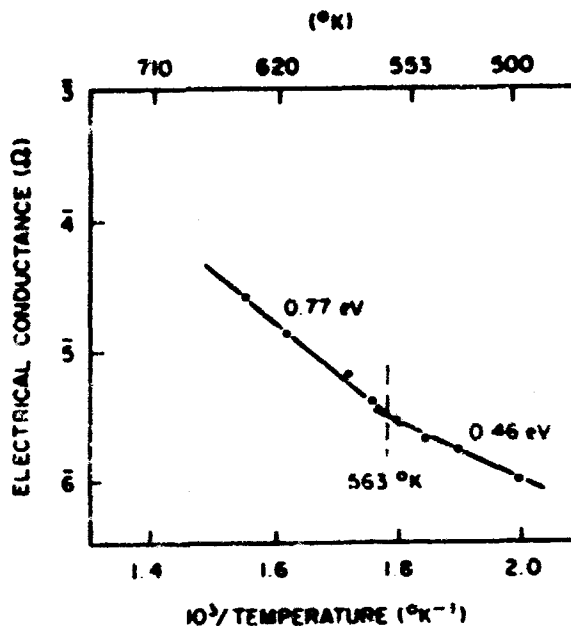


## LEAD OXIDE

### ELECTRICAL CONDUCTIVITY ( $\sigma$ )

log Electrical conductance as a function of reciprocal temperature in lead dioxide, (analytical grade). The change of slope at 563°K (290°C) marks the dissociation temperature of lead dioxide. The slope of the curve is indicated.

(Ref. 10517)

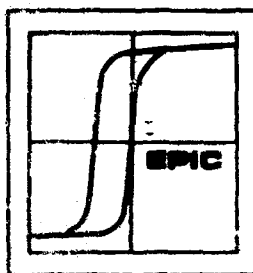


log Electrical conductivity as a function of reciprocal temperature in single crystal red lead monoxide.

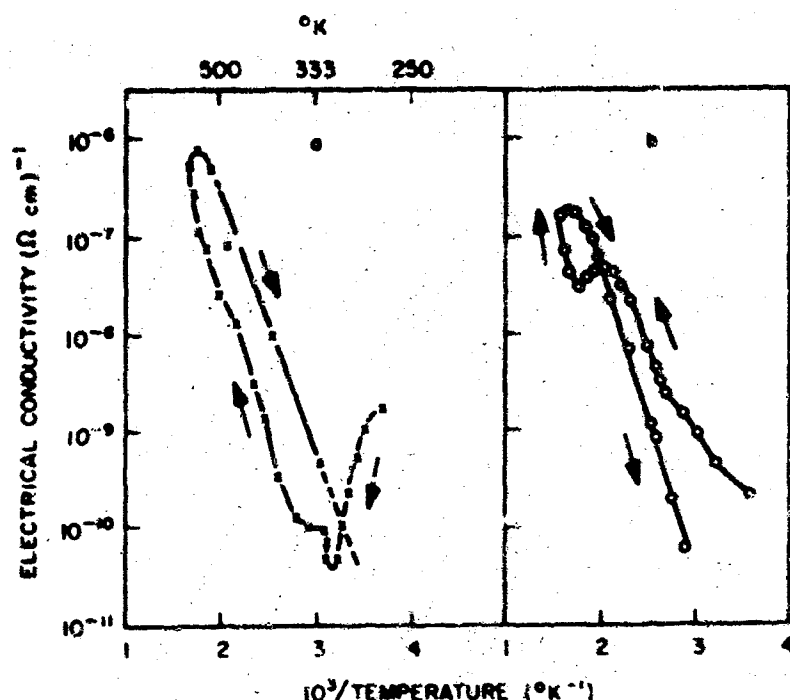
The hysteresis evident in the curves indicates structural rearrangement and absorption processes.

Curve	Slope
AB, A'B',	$\Delta E = 1.25-1.50 \text{ eV}$
CD	$\Delta E = 0.58-0.71 \text{ eV}$

(Ref. 16601)



# LEAD OXIDE ELECTRICAL CONDUCTIVITY ( $\sigma$ )



- a uncoloured sample (no field)
- b coloured sample as a result of illumination in the visible (.4 to .5  $\mu$ ) in an electric field of  $10^3$  V/cm

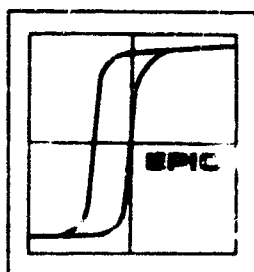
Electrical conductivity as a function of reciprocal temperature in pressed powder lead monoxide pellets. The pellets were activated by annealing.

Colouring is blue, for red lead monoxide, and green, for the yellow lead monoxide. Colour, appearing at places where there are defects, is proportional to field intensity. Heating destroys the colour.

Photosensitivity decreases with the colouring process, and colouring occurs only at wavelengths for which photoconductivity is strong (.436, .546, .579 micron). Colouring also changes the optical properties of the samples as may be seen in the reflectivity spectra.

(Ref. 14622)

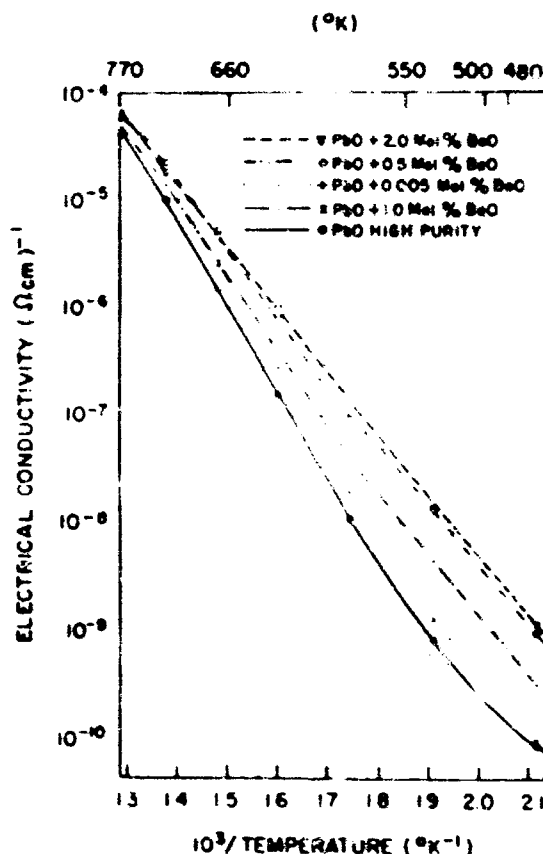
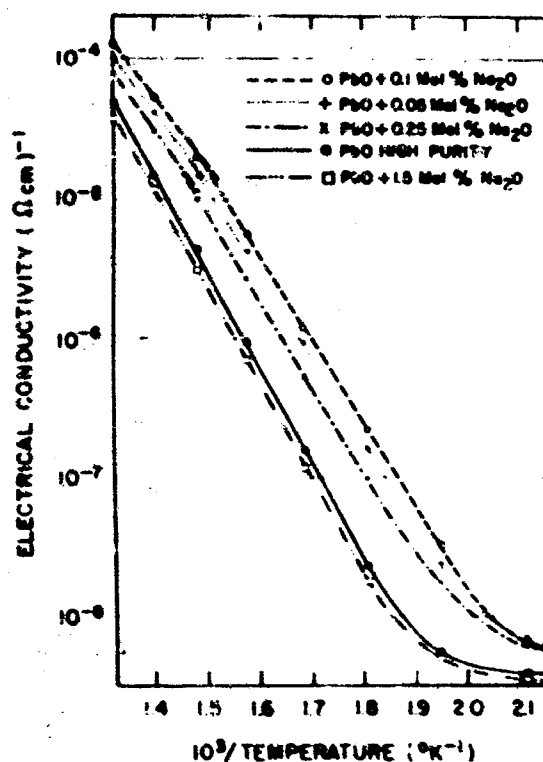




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## LEAD OXIDE

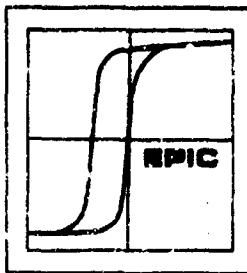
### ELECTRICAL CONDUCTIVITY ( $\sigma$ )



log Electrical conductivity as a function of reciprocal temperature for sintered yellow lead monoxide, variously doped with sodium or barium cations.

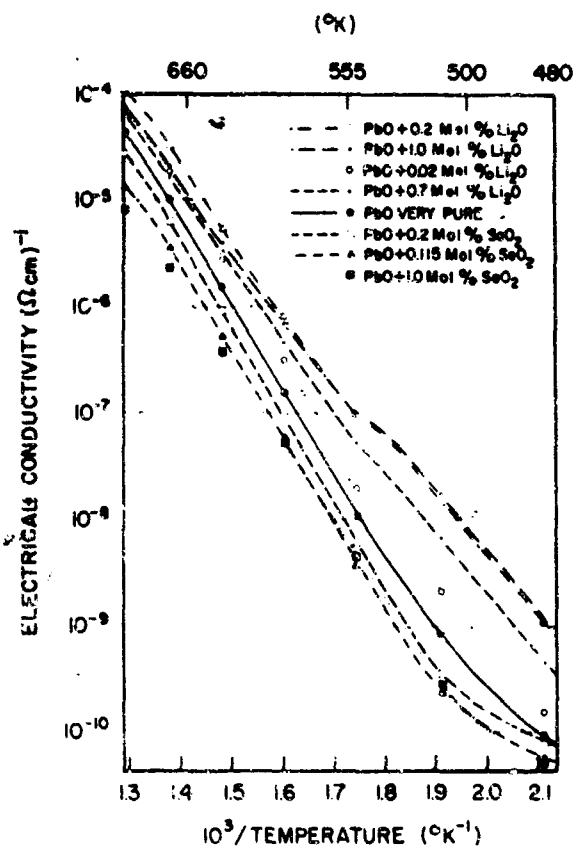
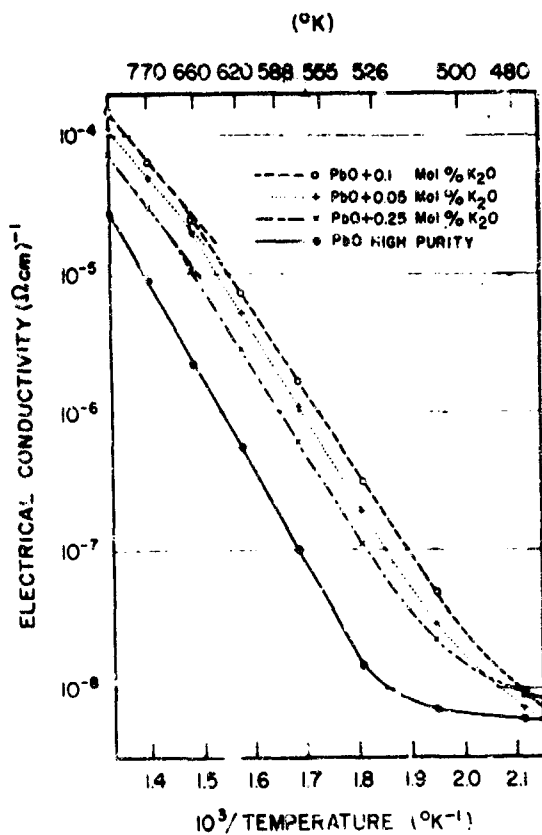
The decisive factors in the activation energy changes are apparently not the nature of the cation but the degree of filling of the oxygen layers as well as the change in interstitial formations by the cations (so called defect order mechanism).

(Ref. 9493)



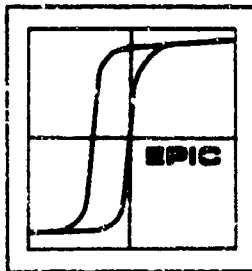
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# LEAD OXIDE ELECTRICAL CONDUCTIVITY ( $\sigma$ )



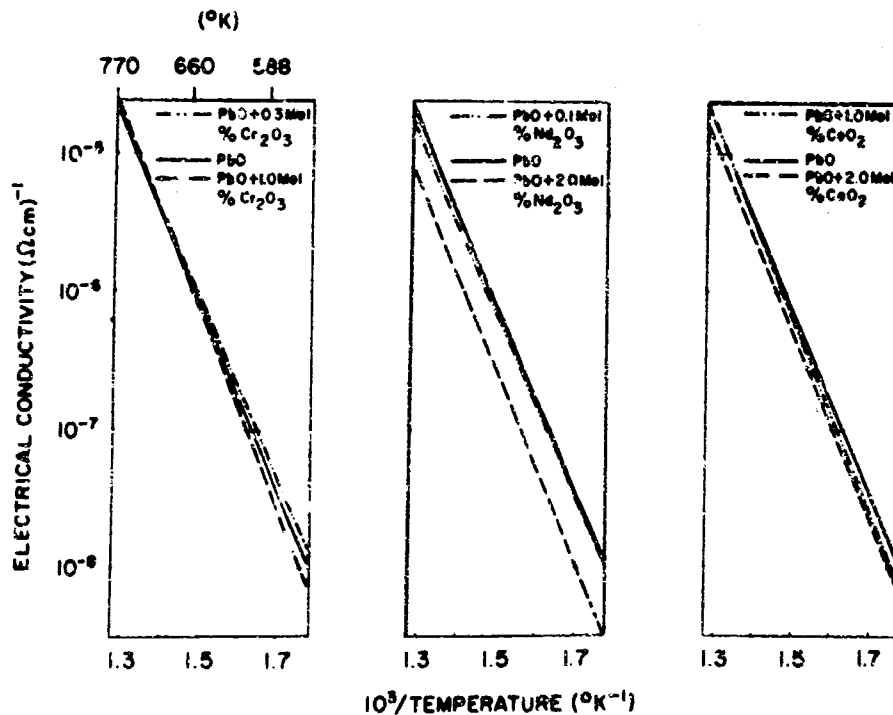
log Electrical conductivity as a function of reciprocal temperature for high purity sintered yellow lead monoxide doped with potassium, lithium or selenium.

(Ref. 9493)



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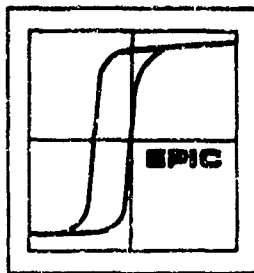
**LEAD OXIDE**  
**ELECTRICAL CONDUCTIVITY ( $\sigma$ )**



log Electrical conductivity as a function of reciprocal temperature for sintered yellow lead monoxide powder pellets, variously doped with chromium, neodymium or cerium.

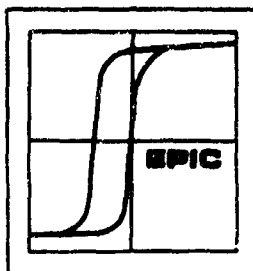
— Undoped commercially pure lead oxide sample shown for comparison.

(Ref. 9493)



LEAD OXIDE  
ELECTRICAL RESISTIVITY ( $\rho$ )

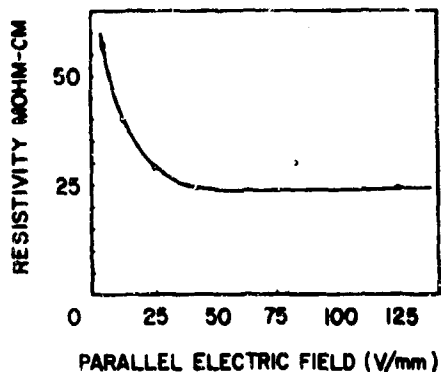
Value ( $\Omega\text{cm}$ )	Sample pressed powder discs	Temperature	Reference
10-15	$\text{PbO}_2$	300°K	14479
$\sim 10^4 - 10^5$	$\text{Pb}_{12}^{0}{}_{19}$	300°K	14479
$\sim 10^{12}$	$\text{Pb}_2^{0}{}_{3}$	300°K	14479
$\sim 10^{12}$	$\text{Pb}_3^{0}{}_{4}$	300°K	14479
$\sim 10^{14}$	PbO (yellow)	300°K	14479



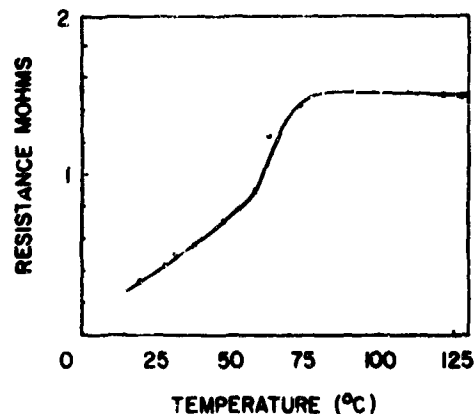
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## LEAD OXIDE

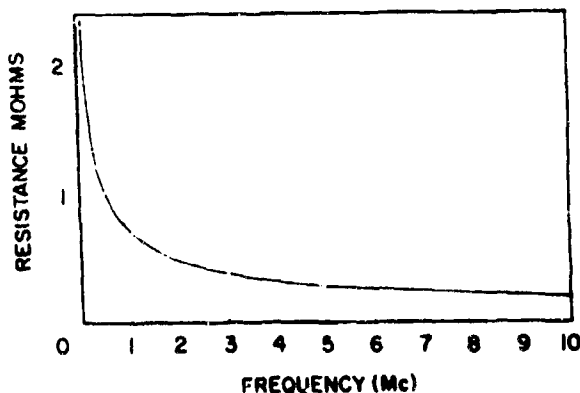
### ELECTRICAL RESISTIVITY ( $\rho$ )



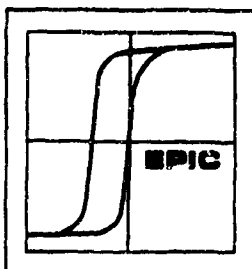
Resistivity as a function of a d. c. electric field applied parallel to the sample of sintered yellow lead monoxide.



Resistance as a function of temperature at 1 kc for the same sample.

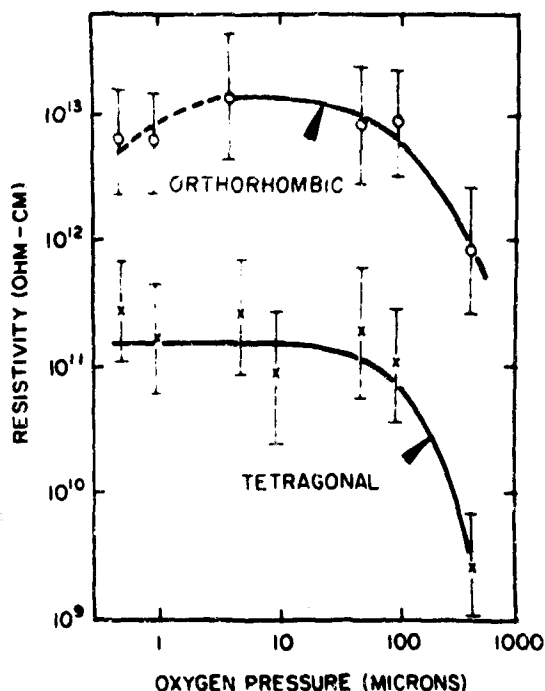


Resistance as a function of frequency to 10 mc for the same sample at 300°K.



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## LEAD OXIDE ELECTRICAL RESISTIVITY ( $\rho$ )



High purity lead oxide films were vapour deposited under oxygen at reduced pressure of 1 micron. These polycrystalline films had crystallites 1-3 microns in size. As deposited, the lead monoxide is always tetragonal. When heat treated at 300°C at 0.5 to 400 microns oxygen pressure, there is a transition to the orthorhombic form.

At lower fields, the slope is 1 indicating ohmic behaviour; at higher fields, the slope is 2 or more, indicating space-charge-limited current.

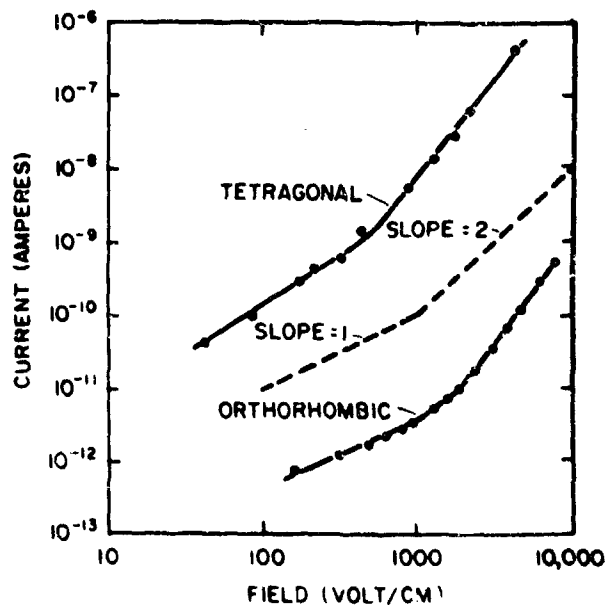
Red lead oxide has a deformed lattice and an active surface and reacts vigorously with oxygen. The lattice is layer type and the ionic distances are short (2.61Å in the yellow and 2.7 in the red).

(Ref. 26041)

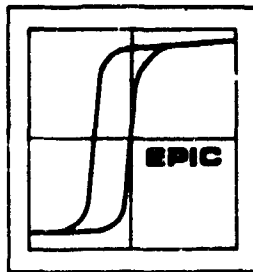
Lead monoxide layers are formed by sputtering lead in an oxygen atmosphere. The original film samples were always n-type, tetragonal in structure as evaporated in a reduced pressure oxygen atmosphere. On annealing, the colour changed to yellow, indicative of the orthorhombic form, and became p-type. The transition occurred as low as 350°C; evidently low oxygen pressure depresses the conversion temperature.

In the tetragonal form, the resistivity is fairly independent of oxygen pressure until it becomes high. In the orthorhombic form, the resistivity is sensitive to the pressure.

Resistivity as a function of oxygen pressure during heat treatment (at 300°C). Measurements taken at 20°C.

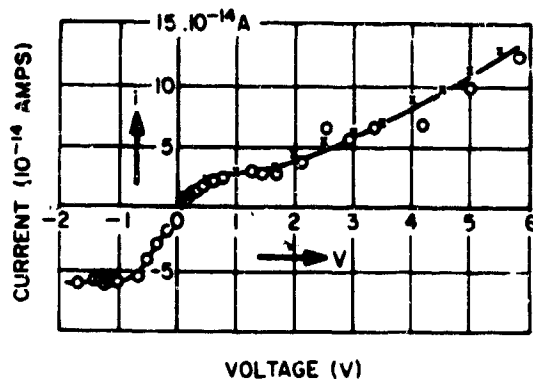


Current-voltage curves taken at 20°C



## LEAD OXIDE

### ELECTRICAL RESISTIVITY ( $\rho$ )



Current-voltage curves for single crystals of red tetragonal lead monoxide.

- o increasing voltage
- + decreasing voltage

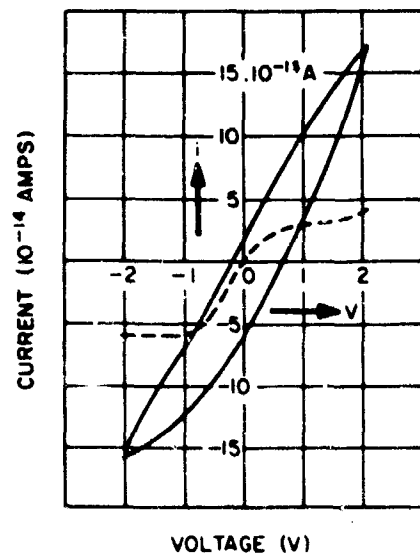
Between -2V and 1.5V, the curve indicates two opposing diodes. At higher voltages a gradual increase of the reverse current is observed. Between 10 and 100V there is a reversible breakdown during which the current increases by several orders of magnitude in a very small voltage range.

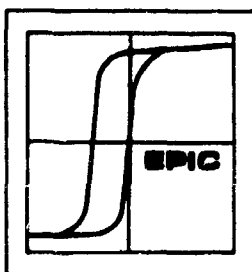
Current voltage curves for the same sample, taken with triangular voltage of  $10^4$ s period. Most of the measured current appears to be due to the charging of the barrier capacitances, which are estimated to be 160pF at 2 V and 125 pF at -2 V.

These values are the lower limits for the true barrier capacitances, since the half period of the voltage (5000 s) is not sufficient to build up the complete barrier change. The lower limits for twelve contacts lie between 50 pF and 1500 pF.

-----static current-voltage curve.

(Ref. 22373)

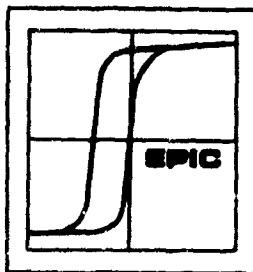




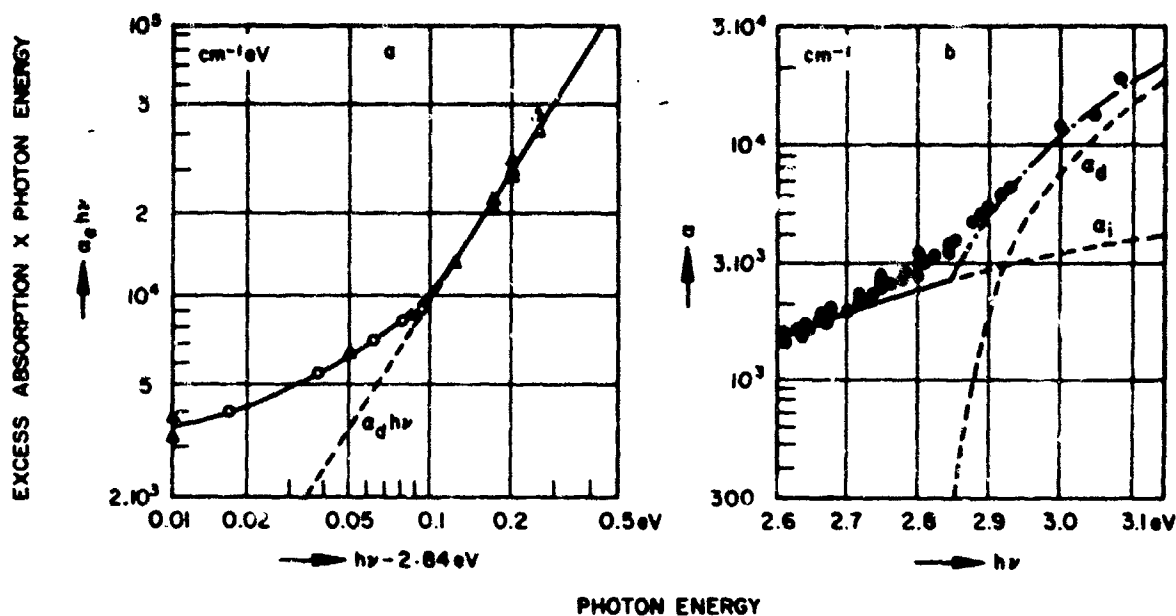
LEAD OXIDE  
ELECTROACOUSTIC PROPERTIES

Symbol	Value (eV)	Sample	Method of Measurement	Temperature (°K)	Reference
LO	0.055	Red, tetragonal single crystal PbO 4-245 $\mu$ thick. n-type, $n = 10^{17} \text{ cm}^{-3}$ . (001) oriented.	Optical absorption, 6530-4000A	133-363	27801
TO	0.034				
Acoustical Phonon	0.013	Red, tetragonal single crystal PbO 4-245 $\mu$ thick. n-type, $n = 10^{17} \text{ cm}^{-3}$ . (001) oriented.	Optical absorption, 6530-4000A	133-363	27801
Optical Phonon	0.030	Red, tetragonal single crystal PbO 4-245 $\mu$ thick. n-type, $n = 10^{17} \text{ cm}^{-3}$ . (001) oriented.	Optical absorption, 6530-3000A	133-363	27801
Photon Branch	0.01	Yellow PbO platelets 0.1 - 0.2 mm thick.	Thermal conductivity 0-200°C		27776
LO is the longitudinal optical phonon branch. TO is the transverse optical phonon branch.					





# LEAD OXIDE ELECTROACOUSTIC PROPERTIES



a normalized absorption coefficient

b absorption coefficient of initial and excess absorption as calculated and their sum as measured.

Absorption curve above  $\alpha = 1000 \text{ cm}^{-1}$  as a sum of contribution from the indirect transition:

$$\alpha_i = 8.8 \times 10^3 (\text{h}\nu)^{-1} (\text{h}\nu - 1.94 \text{ eV})^2 \text{ cm}^{-1}$$

and from direct transitions:

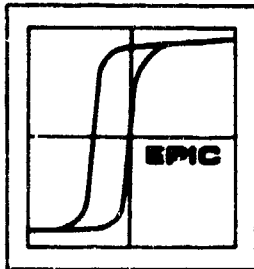
$$\alpha_d = 3.3 \times 10^5 (\text{h}\nu)^{-1} (\text{h}\nu - 2.84 \text{ eV})^{1.5} \text{ cm}^{-1}$$

$\alpha$  and  $\Delta$  = values in crystals 4 and  $8.7 \mu$  thick less  $\alpha_i \text{ h}\nu$

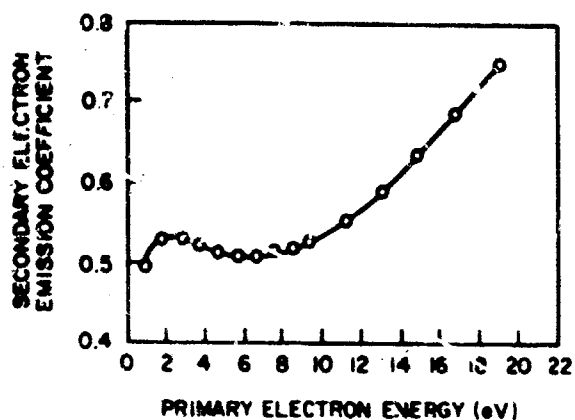
$\alpha_i$  = initial absorption

$\alpha_d$  = excess absorption

(Ref. 27801)

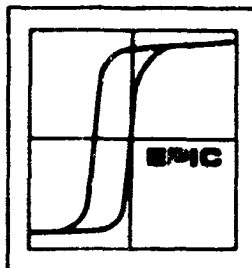


LEAD OXIDE  
ELECTRON SECONDARY EMISSION



Secondary electron emission coefficient as a function of primary electron energy in vacuum deposited lead monoxide films, oxidized after evaporation by heating in oxygen at 400°C. (The maximum coefficient is 1.2 - 2.0). From theoretical considerations, the photoelectric work function is assumed to be larger than 3 eV.

(Ref. 21307)

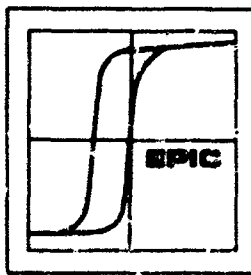


**LEAD OXIDE**  
**ENERGY BANDS**

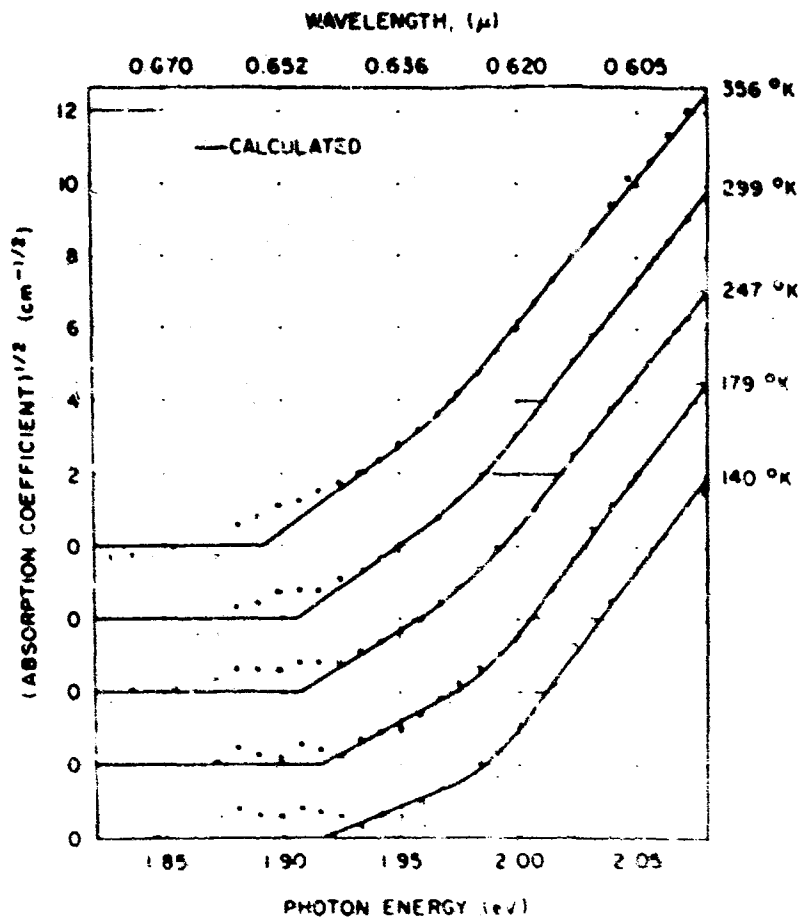
Symbol	Value ( $10^{-4}$ eV/ $^{\circ}$ K)	Sample	Method of Measurement	Temperature ( $^{\circ}$ K)	Reference
$dE_{g2}/dT^*$	-(1.32)	Red, tetragonal PbO single crystal plates, 4-245 $\mu$ thick, (001) oriented, n-type $n = 10^{17}$ cm $^{-3}$	Optical absorption $\lambda = 0.65-0.40\mu$ $T = 133^{\circ}-363^{\circ}$ K	300	27801
$dE_{g1}/dT$	-(1.0 $\pm$ 0.1)	Red, tetragonal PbO, annealed at 600 $^{\circ}$ K	Diffuse reflection $\lambda = 0.4-0.7\mu$	290-573	14605
$dE_{g2}/dT^{**}$	-(8.0 $\pm$ 1.0)	Red, tetragonal PbO, annealed at 600 $^{\circ}$ K	Diffuse reflection $\lambda = 0.4-0.7\mu$	290-573	14605
$dE_g/dT^{**}$	-(11.5 $\pm$ 1)	Yellow, PbO orthorhombic	Diffuse reflection $\lambda = 0.4-0.7\mu$	290-573	14605
$dE_{g1}/dT$	-(3.0 $\pm$ 1.0)	Red PbO, not annealed, (irreversible change)	Diffuse reflection $\lambda = 4.7\mu$	290-400	14605
$dE_{g1}/dT$	-(1.4 $\pm$ 0.5)	Continued heating to 573 $^{\circ}$ K, (reversible change)	Diffuse reflection $\lambda = 4.7\mu$	400-573	14605
$dE_{g2}/dT$	-(3 $\pm$ 1)	Continued heating to 573 $^{\circ}$ K, (reversible change)	Diffuse reflection $\lambda = 4.7\mu$	400-573	14605

\* $E_{g2} = 1.952 - (2.2 \times 10^{-7} T^2)$  eV from 133 $^{\circ}$  K - 363 $^{\circ}$  K. The derivative of the indirect band gap at 300 $^{\circ}$  K is as given above.

\*\*Shift in energy gap with temperature of these two forms is practically an order of magnitude greater than for the majority of semiconductors.



# LEAD OXIDE ENERGY BANDS

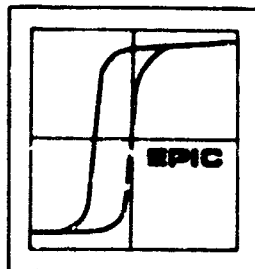


Absorption coefficient as a function of photon energy in tetragonal lead monoxide near the absorption edge, for several temperatures.

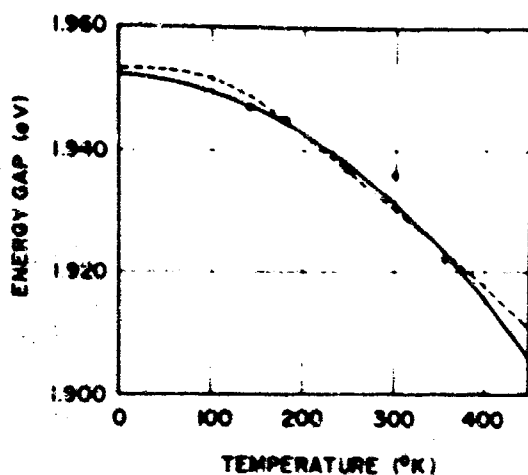
Single crystals were grown hydrothermally and the transparent red platelets were from 4 - 245  $\mu$  thick. Crystals were generally n-type,  $n = 10^{17} \text{ cm}^{-3}$  and (001) oriented. Illumination parallel to (001) from 6530 to 4000 Å.

The vertical scales have been shifted over  $2 \text{ cm}^{-1/2}$  for the different temperatures. The measurements indicated with dots have not been included in the final least-square fit. If, with  $h\nu < 1.88 \text{ eV}$ , the measured transmitted intensity exceeds the calculated one, the  $a^{1/2}$  value has been drawn as negative.

(Ref. 27801)



# LEAD OXIDE ENERGY BANDS



Energy gap as a function of temperature for samples shown on previous page.

—  $E_g = 1.952 - 2.2 \times 10^{-7} T^2$  eV

---  $E_g = 1.953 - 0.05 (\exp(50/T) - 1)^{-1}$  eV

$E_g$  is the indirect band gap.

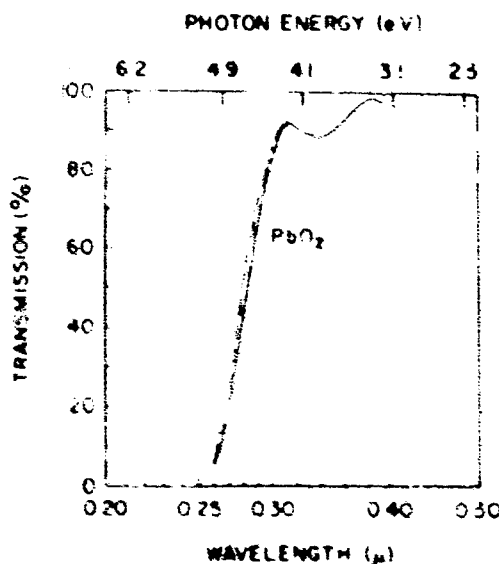
(Ref. 27801)

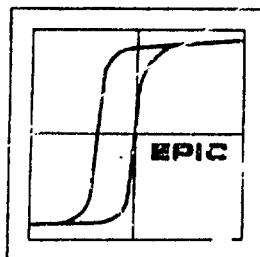
Shift in transmission as a function of wavelength with temperature for lead dioxide.

— 303°K

--- 128°K

(Ref. 3281)

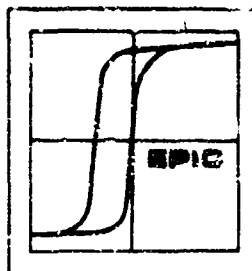




LEAD OXIDE  
ENERGY GAP

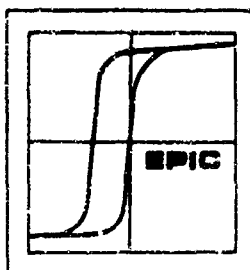
Symbol	Value (eV)	Sample	Method of Measurement	Temperature (°K)	Reference
$E_{g1}$ (Direct)	$2.84 \pm 0.03$	Red, tetragonal PbO single crystal plates, 4-245 $\mu$ thick, (001) oriented, n-type, $n = 10^{17} \text{ cm}^{-3}$	Optical absorption $\lambda = 0.65-0.40 \mu$ Incident light parallel (001) $T = 300^\circ\text{K}$	300	27801
$E_{g2}$ (Indirect)	$1.936 \pm 0.01$	Red, tetragonal PbO single crystal plates, 4-245 $\mu$ thick, (001) oriented, n-type, $n = 10^{17} \text{ cm}^{-3}$	Optical absorption $\lambda = 0.65-0.40 \mu$ Incident light parallel (001) $T = 300^\circ\text{K}$	300	27801
$E_{g2}$	$2.1 \pm 0.03$	Red PbO powder	Diffuse reflection $\lambda = 0.4-0.7 \mu$ $T = 290-573^\circ\text{K}$	0	14605*
$E_{g1}$	$3.15 \pm 0.05$	Red PbO powder	Diffuse reflection $\lambda = 0.4-0.7 \mu$ $T = 290-573^\circ\text{K}$	0	14605*
$E_{g2}$	$2.07 \pm 0.03$	Red PbO powder	Diffuse reflection $\lambda = 0.4-0.7 \mu$ $T = 290-573^\circ\text{K}$	300	14605*
$E_{g1}$	$2.92 \pm 0.03$	Red PbO powder	Diffuse reflection $\lambda = 0.4-0.7 \mu$ $T = 290-573^\circ\text{K}$	300	14605*

\*This author suggested that the two energy band values  $E_{g1}$  and  $E_{g2}$  with a difference of about 1 eV might be due to the presence of yellow PbO impurities present in the red form. However, the most recent work shown in Ref. 27801 indicates that the smaller value is the indirect transition and the larger value is the direct transition on the assumption that two different conduction (or valence) bands are involved.



LEAD OXIDE  
ENERGY GAP

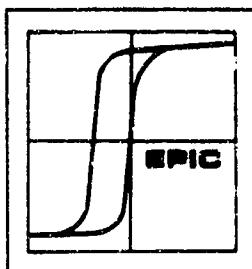
Symbol	Value (eV)	Sample	Method of Measurement	Temperature (°K)	Reference
$E_{g1}$	$2.17 \pm 0.03$	Red PbO powder unannealed	Diffuse reflection $\lambda = 0.4 - 0.7 \mu$ $T = 290 - 573^\circ K$	0	14605
$E_{g1}$	$2.1 \pm 0.04$	Red PbO powder unannealed	Diffuse reflection $\lambda = 0.4 - 0.7 \mu$ $T = 290 - 573^\circ K$	0	14605
$E_{g2}$	$3.0 \pm 0.1$	Red PbO powder heated, (reversible change)	Diffuse reflection $\lambda = 0.4 - 0.7 \mu$ $T = 290 - 573^\circ K$	0	14605



LEAD OXIDE  
ENERGY GAP

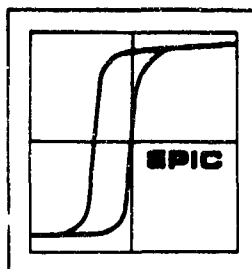
Symbol	Value (eV)	Sample	Method of Measurement	Temperature (°K)	Reference
$E_g$	3.0	PbO, yellow single crystals	Optical absorption $\lambda = 0.4-0.5 \mu$	300	16327
$E_g$	$1.96 \pm 0.06$	PbO, yellow single crystal photoconductive	Optical transmission $\lambda = 0.4-0.7 \mu$	300	16601
$E_g$	$\sim 1.9$	PbO, yellow single crystal photoconductive	Photoconductivity maximum at $0.61 \mu$	300	16601
$E_g$	$3.1 \pm 0.1$	Yellow PbO powder	Diffuse reflection $\lambda = 0.1-0.7 \mu$ $T = 290-573^\circ K$	0	14605
$E_g$	3.2	pure, yellow PbO powder	Electrical resistivity	0	9493
		PbO polycrystalline films, reduced oxygen pressure, $50-75 \mu$ thick			
$E_g$	2.0	red tetragonal	Photoconductivity maximum	300	26041
$E_g$	2.6	yellow orthorhombic	Photoconductivity maximum	300	26041
$E_g$	2.0	red tetragonal	Optical absorption $\lambda = 0.35-0.65 \mu$	300	26041
$E_g$	2.6	yellow orthorhombic	Optical absorption $\lambda = 0.35-0.65 \mu$	300	26041





LEAD OXIDE  
ENERGY GAP

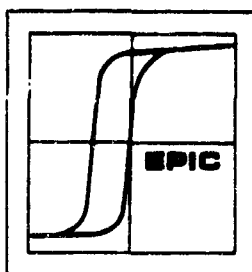
Symbol	Value (eV)	Sample	Method of Measurement	Temperature (°K)	Reference
$E_g$	2.6	PbO poly-crystalline films, yellow, 11.6 $\mu$ particle size	Diffuse reflection $\lambda = 0.4 - 0.8 \mu$	300	14606
$E_g$	1.9	red, photo-sensitive 7.7 $\mu$ particle size	Diffuse reflection $\lambda = 0.4 - 0.8 \mu$	300	14606
$E_g$	2.2	red, photo-sensitive 7.7 $\mu$ particle size	Diffuse reflection $\lambda = 0.4 - 0.8 \mu$	300	14606
$E_g$	$4.45 \pm 0.032$	PbO <sub>2</sub> film, vacuum deposited	Optical absorption $\lambda = 0.41 - 0.25 \mu$	300	3281



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LEAD OXIDE  
ENERGY LEVELS

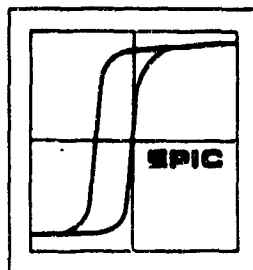
Symbol	Value (eV)	Sample	Method of Measurement	Temperature (°K)	Reference
$E_F$ (PbO surface state)	0.95 <sub>CB</sub>	Single, crystal, red, tetragonal, n-type, PbO, (001) oriented, $n = 10^{17} \text{ cm}^{-3}$	Photoconductivity long-wavelength limit	300	22373
$E_D$	0.5 <div>Dopant Bi</div>	PbO films, Bi-doped yields n-type, Tl-doped is p-type	Photoconductivity at $\lambda = 5950\text{\AA}$ , increases sharply in doped films, depending on illumination intensity and temperature	293	16794
$E_D$	1.33 Oxygen	Red, tetragonal PbO layered crystal lattice is filled with oxygen and degree of filling determines the film photosensitivity	Photoconductivity	300	14606
$E_A$	~2.3 Li, K, Na	Yellow PbO sintered pellets	Electrical conductivity	275	2424



**LEAD OXIDE**  
**ENERGY LEVELS**

Symbol	Value (eV)	Sample	Method of Measurement	Temperature (°K)	Reference
$E_i$	1.48-1.52	Yellow PbO films, 1-3 $\mu$ thick, vacuum-deposited and not photo-sensitive $\rho = 10^9 - 10^{10} \Omega \text{cm}$	Electrical conductivity	300-673	3551
$E_i$	2.0-2.2	Orange PbO films after heating to 450°C in air become photo-sensitive at $\lambda = 0.4 - 0.7 \mu$ $\rho = 10^9 - 10^{10} \Omega \text{cm}$	Electrical conductivity	300-673	3551
$E_D$ , electron ionization level $E_A$ , hole ionization level $E_i$ , ionization or activation level $E_F$ , Fermi level					

**AIR FORCE MATERIALS LABORATORY**  
RESEARCH AND TECHNOLOGY DIVISION  
AIR FORCE SYSTEMS COMMAND

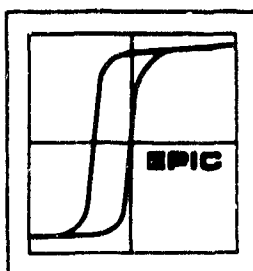


**E**LECTRONIC  
**P**ROPERTIES  
**I**NFORMATION  
**C**ENTER

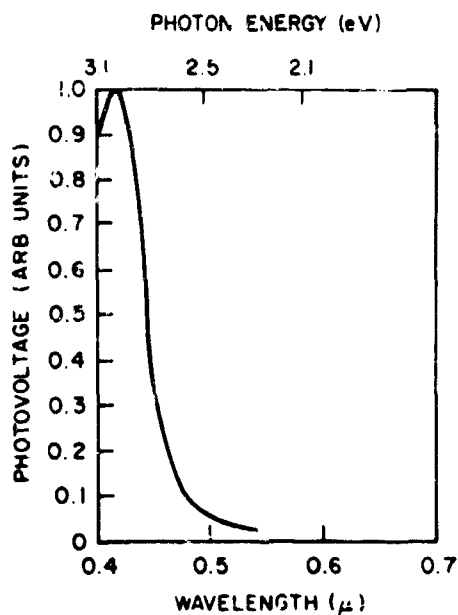
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LEAD OXIDE  
MAGNETIC SUSCEPTIBILITY ( $\chi$ )

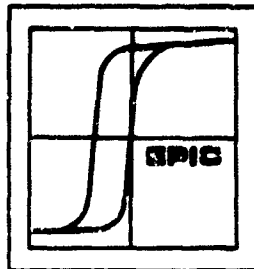
Value	Sample	Temperature	Reference
$-42.0 \times 10^{-6}$ cgs	PbO	300°K	Handbook of Chem. and Phys. 47th Ed. 1966-1967. p. E-105.



LEAD OXIDE  
PHOTOELECTRONIC PROPERTIES

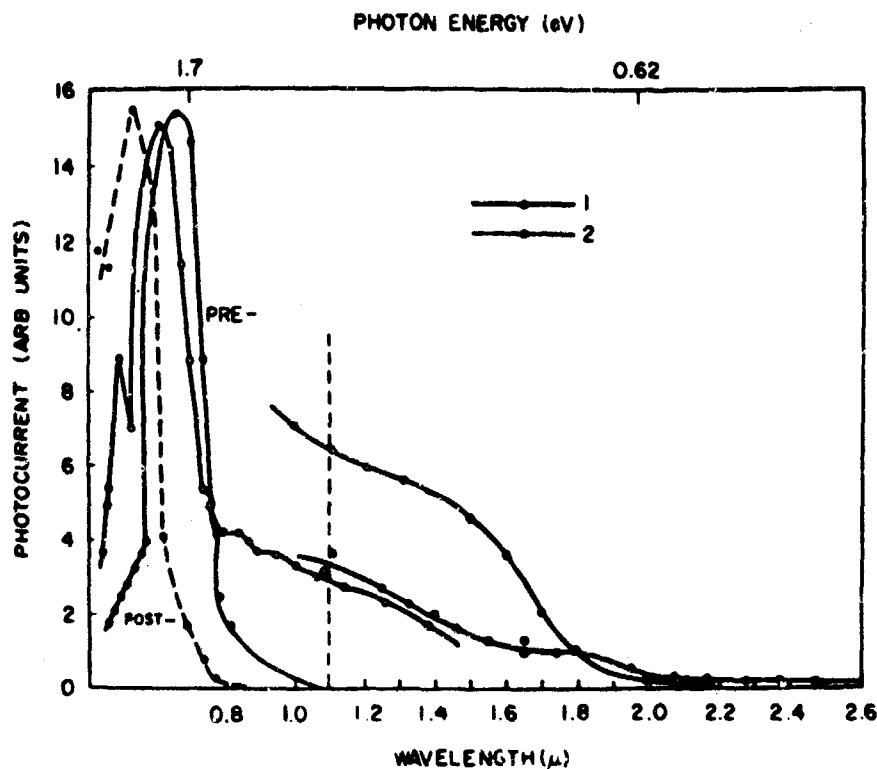


Photovoltage as a function of wavelength in lead monoxide powder.



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## LEAD OXIDE PHOTOELECTRONIC PROPERTIES

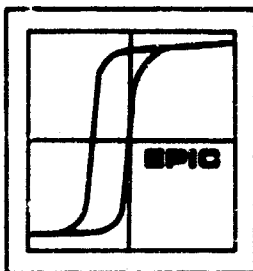


Photocurrent as a function of wavelength in lead monoxide films at 300°K, variously treated. Thickness = 1 - 3 microns,  $\rho = 10^9 - 10^{10} \Omega\text{cm}$ .

- Annealed at 450°C
- 1. Sulfur-treated and then heated in air
  - 2. Selenium-treated and then heated in air

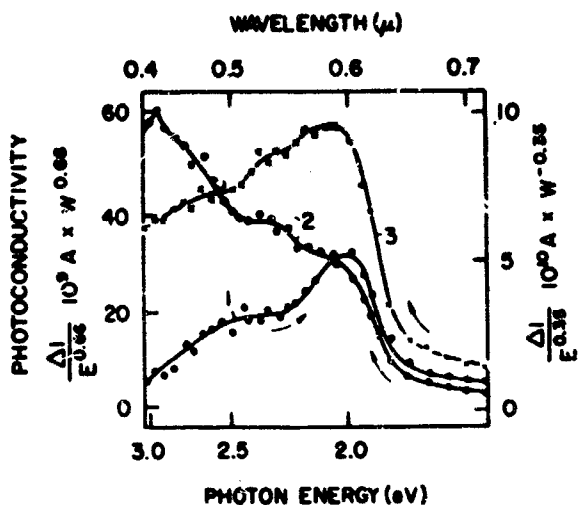
The right hand portion of the graph shows the long wavelength portion of the curve on an enlarged scale. Electrical resistivity of the material is not materially changed by the treatment, but the photosensitivity is greatly increased. Evidently the photosensitivity is caused by introduction of sulfur and selenium atoms into the lead oxide lattice.

(Ref. 3551)



## LEAD OXIDE

### PHOTOELECTRONIC PROPERTIES



$\Delta I$  is the non-linear photoconductivity ( $\Delta I \sim L^x$ ) and the index  $x$  equals 0.66 for low illumination and 0.35 for higher intensities. The index also varies with application of intensity and the curve is hysteretic. There is also a relative increase in the short-wave spectrum. All these variations are apparently the result of surface changes.

(Ref. 16601)

Photoconductivity as a function of photon energy in single crystal lead monoxide, both red and yellow,

$$\rho = 10^{10} - 10^{12} \Omega \text{cm}$$

$$T = 300^\circ \text{K}$$

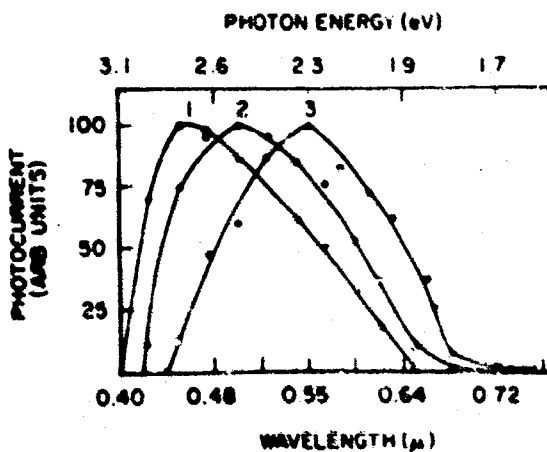
Curves 1, 2 and 3 are variously illuminated and recorded.

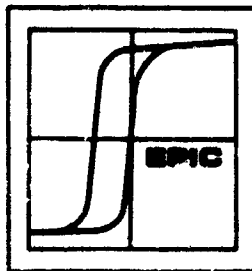
Yellow lead monoxide films, vapor-deposited at high temperature in oxygen, were further annealed at  $400^\circ \text{C}$ .

The shift of the photoconductivity maximum to the red with increasing thickness is probably a result of increased absorption at long wavelengths.

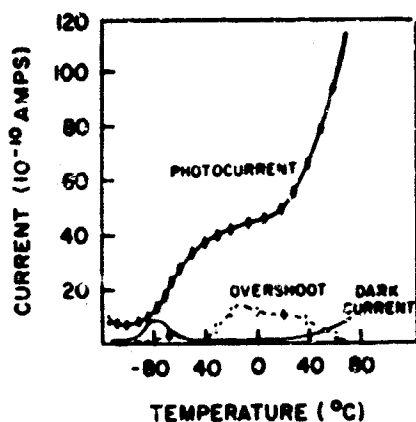
Photocurrent as a function of wavelength in lead monoxide films of several thicknesses.

1.  $1.6 \mu$
2.  $5.4 \mu$
3.  $11 \mu$





## LEAD OXIDE PHOTOELECTRONIC PROPERTIES



Lead monoxide films are irradiated with x-rays under a dc electric field. The current through the layer rises to a maximum and then decays to a minimum. At this point, if irradiation ceases, there is further decay to normal dark current. Onset of irradiation now initiates photocurrent or, depending on several variables can cause overshoot as a result of electronic processes, in the bulk material.

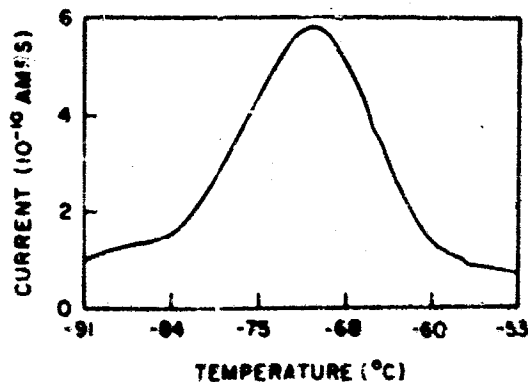
Current as a function of temperature for lead monoxide films.

1. Photocurrent at steady state
2. Overshoot
3. Dark current

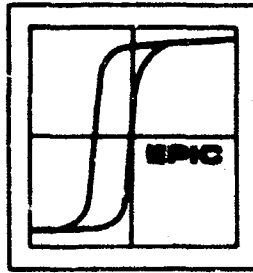
These curves shift, depending on sample preparation but in general remain relatively similar.

Lead monoxide film is cooled to  $-103^{\circ}\text{C}$  and irradiated by x-rays. Current is measured during warming, at 230V. The curve indicates that trap levels are concentrated below the conduction band from  $-50$  to  $-85^{\circ}\text{C}$ , the temperature range which shows overshoot (see above). At higher temperatures, the holes become mobile and leak off at the electrodes; there is no space charge build-up and photocurrent increases. At lower temperatures overshoot disappears and photocurrent decreases as a result of higher trapping and recombination rates.

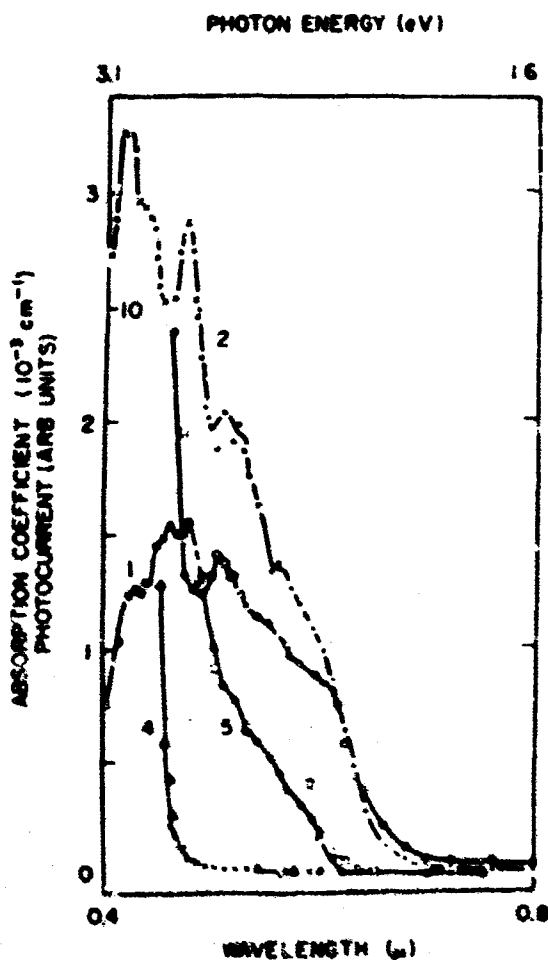
(Ref. 5894)







## LEAD OXIDE PHOTOELECTRONIC PROPERTIES



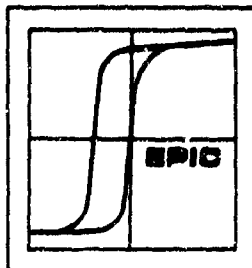
The photosensitivity of the surface layer of polycrystalline red lead oxide powder is compared to the absorption spectra as a function of wavelength at 300°K.

- |   | particle size |
|---|---------------|
| o 1. Photocurrent intensity of the red monoxide                                   | 7.7 $\mu$     |
| x 2. Photocurrent intensity with illumination applied with a reversal in spectrum |               |
| 4. Absorption coefficient for yellow lead monoxide powder                         | 11.6 $\mu$    |
| +   | calculated    |
| $\Delta$  | experimental  |
| 5. Absorption coefficient for red powder  |               |
| ●   | calculated    |
| □   | experimental  |

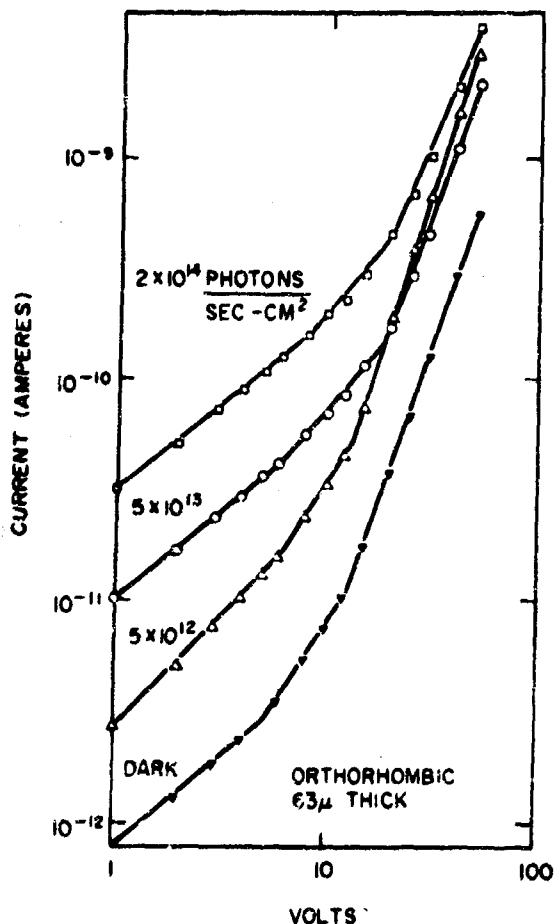
Considerable photoeffect is observed in the red oxide at the edge of the inherent absorption and is indicative of an additional absorption band in the .46 to .65 micron region.

Oxygen is first absorbed on the surface of the sample, leading to the formation of surface impurity states which latter initiate the photoeffects in the long wavelengths. In addition, as the oxygen is introduced into the lattice, photoconductivity is further increased.

(Ref. 14606)



## LEAD OXIDE PHOTOELECTRONIC PROPERTIES



Photocurrent as a function of voltage in tetragonal and orthorhombic lead monoxide films.

The films were heat-treated at 300°C under 1 micron oxygen pressure.

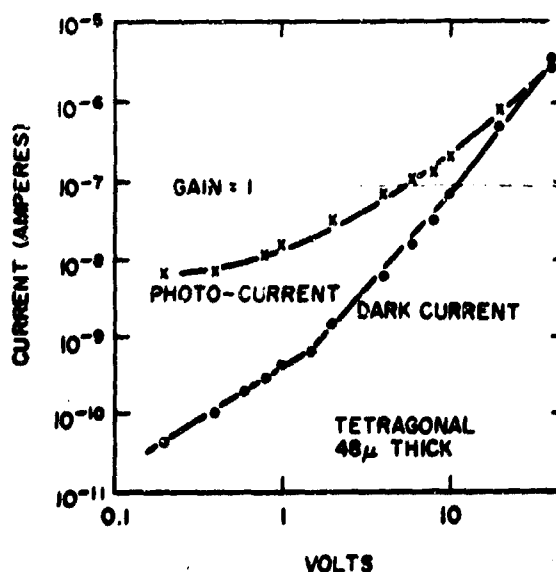
Measurements taken at

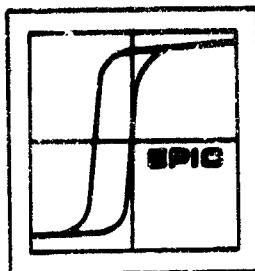
$$\lambda = 5600\text{\AA}$$

(Ref. 26041)

When photocurrent is measured as a function of voltage, an upper limit of photosensitivity is attained at which the photocurrent cannot be distinguished from the dark current. The dotted line indicates the current level at which the quantum gain (carrier pairs/produced/photons absorbed) is equal to 1.

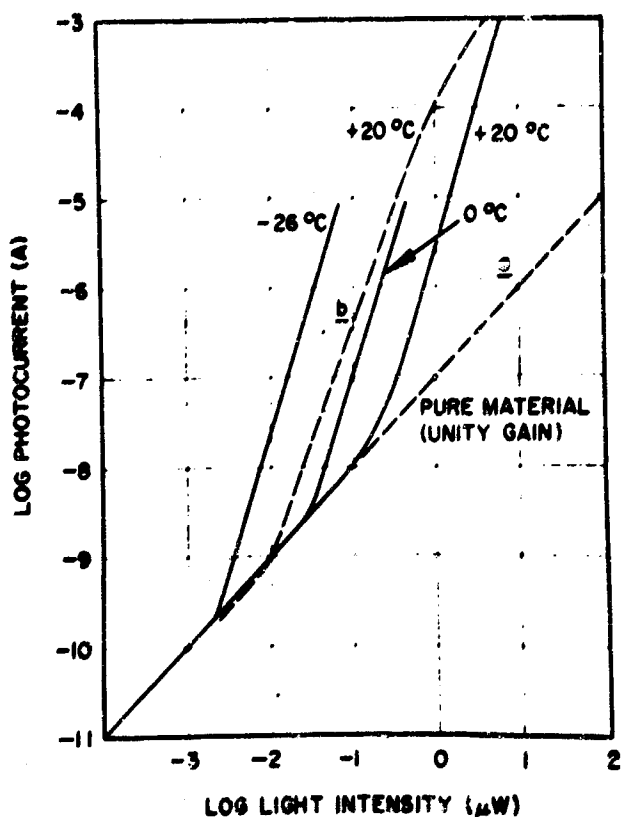
Behaviour may be explained by the fact that at high applied fields, photocurrents are comparable to the space-charge-limited dark current.





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# LEAD OXIDE PHOTOELECTRONIC PROPERTIES



log Photocurrent as a function of log light intensity in bismuth-thallium doped lead monoxide films at several temperatures, as indicated on the curves.

- a. pure material
- b. slightly more of the bismuth and thallium dopant increases activation

Measurements taken at

$$\lambda = 5950 \text{ \AA}$$

(Ref. 16794)

Photocurrent as a function of light intensity for a red tetragonal lead monoxide film.

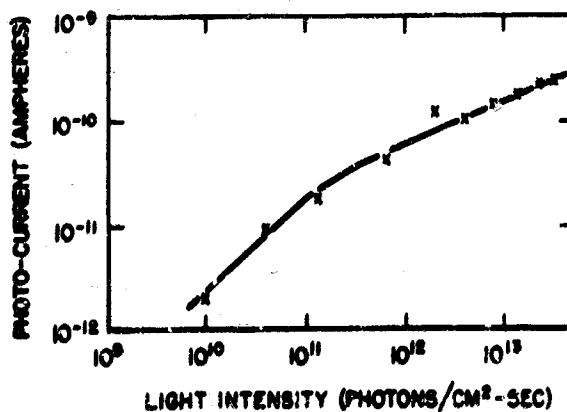
Oxygen pressure during heat treatment at 300°C was 5 microns. Film thickness is 63 microns.

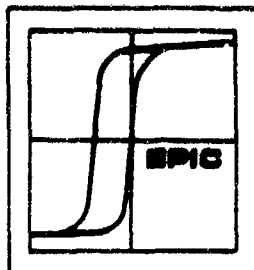
Measurements taken at

$$\lambda = 5600 \text{ \AA}$$

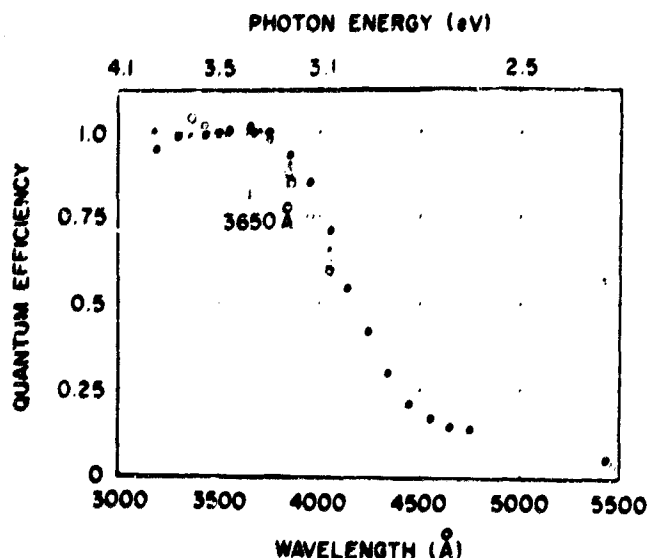
and 0.6V

(Ref. 26041)





## LEAD OXIDE PHOTOELECTRONIC PROPERTIES



Quantum gain, (or efficiency) = (carrier pairs produced/photons absorbed) as a function of wavelength in single crystal red lead monoxide (100  $\mu$  thick).

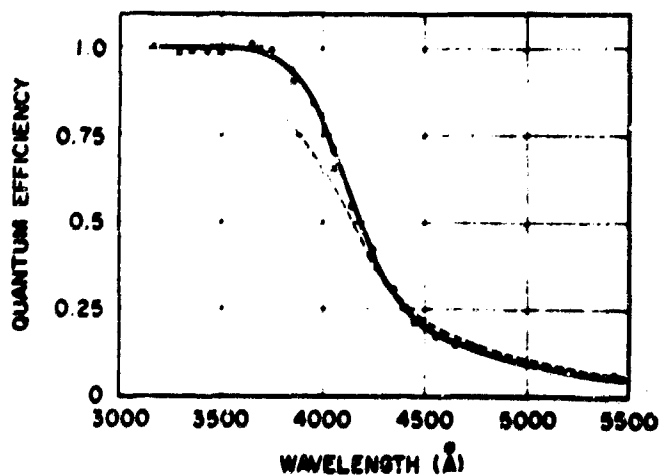
The quantum efficiency is at a maximum and constant from 3800 to 3100 Å.

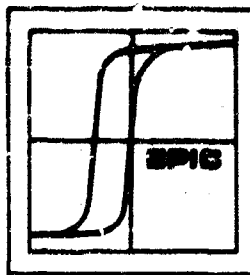
(Ref. 25706)

Quantum efficiency as a function of wavelength in red lead monoxide photodetector. Bulk resistivity =  $10^3$ - $10^4$   $\Omega$ cm 10 Volts, illumination normal to sample.

----- Theoretical curve calculated from barrier width, absorption coefficient and carrier diffusion length. Values used are  $L = 1.2 \mu$ ,  $B = 1 \mu$  (corresponding to a hole concentration  $n_p = 2 \times 10^{16} \text{ cm}^{-3}$ ).

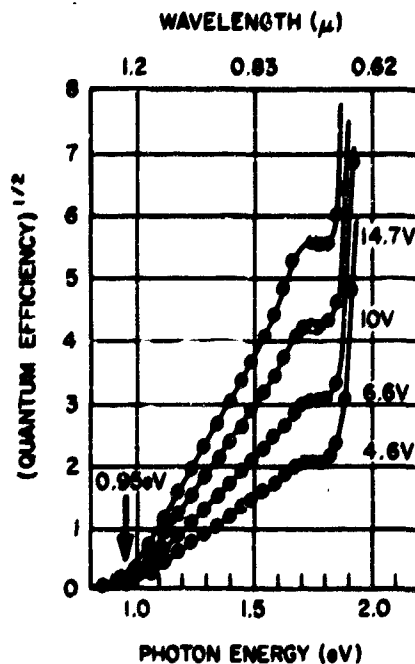
(Ref. 25717)





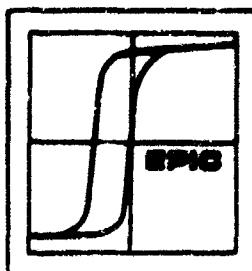
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**LEAD OXIDE  
PHOTOELECTRONIC PROPERTIES**



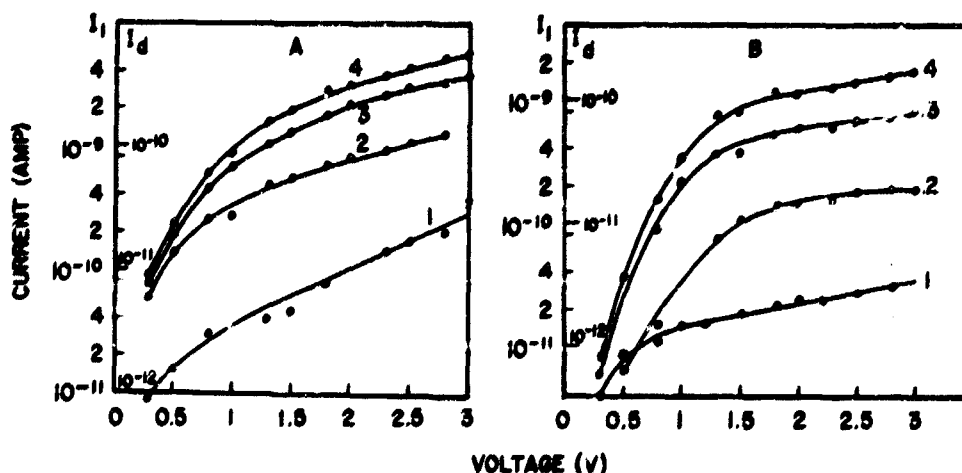
The square root of the quantum efficiency as a function of photon energy in a red lead photo diode. The threshold energy is indicated at 0.95 eV. The reverse voltages are indicated on the curves. These values give a calculated barrier width of about 0.1 micron and an electron mean free path equal to 0.01 microns.  $n_n = 10^{17} \text{ cm}^{-3}$ .

(Ref. 22373)



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## LEAD OXIDE PHOTOELECTRONIC PROPERTIES



Current-voltage curves for yellow lead monoxide films vapour-deposited from the yellow powder in a vacuum or formed in situ by evaporation of lead in oxygen atmosphere. Film thickness varied from 0.5 to 10 microns. Resistivity from  $10^{12}$  to  $10^{13}$   $\Omega\text{cm}$ .

$I_d$  dark current

$I_l$  photocurrent

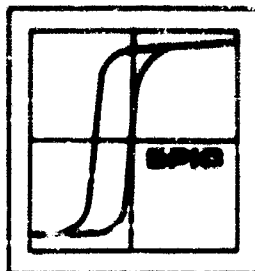
It was possible to change the polarity of the substrata and:

A positive substrate (in relation to film)

B negative substrate (in relation to film)

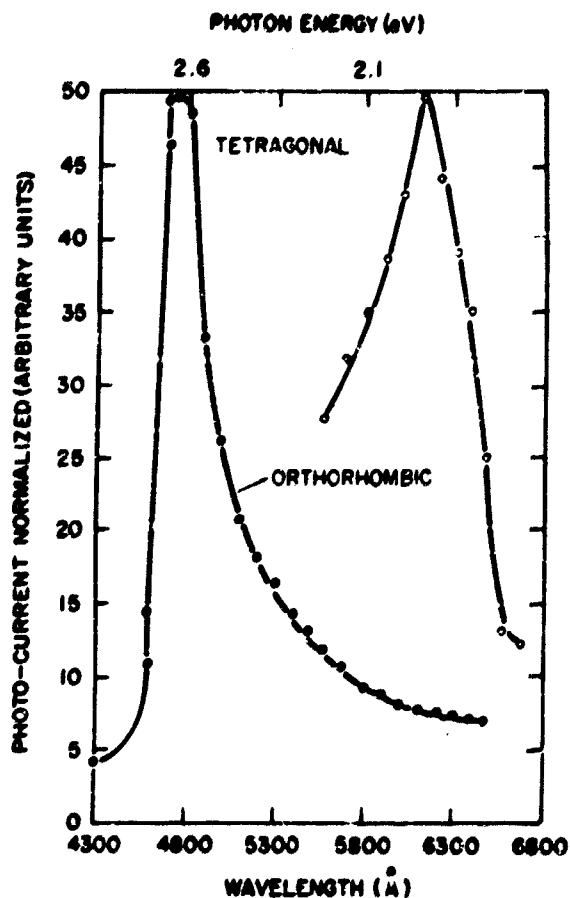
1. dark current
2. 38 lux illumination intensity
3. 216 lux illumination intensity
4. 420 lux illumination intensity

(Ref. 3421)



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# **LEAD OXIDE** **PHOTOELECTRONIC PROPERTIES**



Photocurrent as a function of wavelength in tetragonal and orthorhombic lead monoxide films.

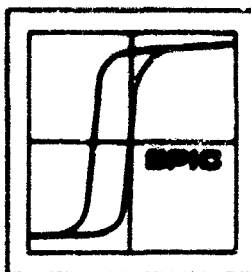
**Tetragonal:** Heat treated at 300°C and 0.5 micron oxygen pressure.  
0.54 microns thick.  
Voltage = 1<sup>0</sup> V.

**Orthorhombic:** Heat-treated at 300°C and 100 microns oxygen pressure.  
89 microns thick.  
Voltage = 10 V.

Light intensity is approximately equal for the two types of film.

(Ref. 26041)

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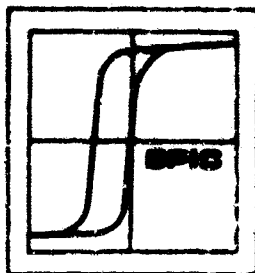
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**LEAD OXIDE  
RICHARDSON'S CONSTANT (A)**

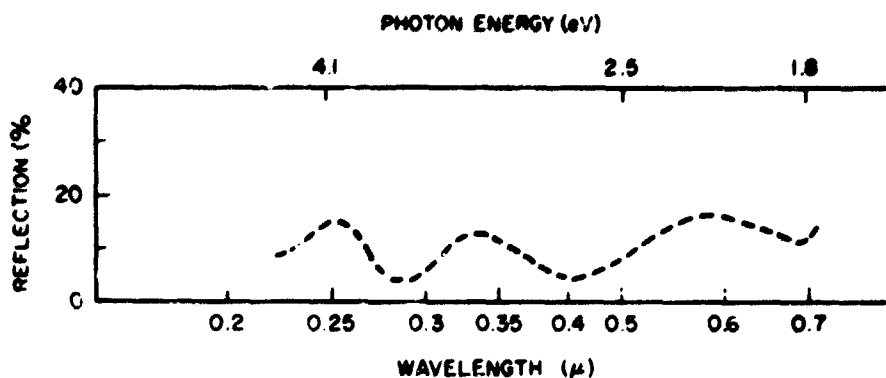
Value	Sample	Reference
$120\text{A}/\text{cm}^2\text{K}^2$	Red tetragonal, single crystal, n-type PbO cleaved on (001) plane, $n_n \sim 10^{17}\text{cm}^{-3}$	22373



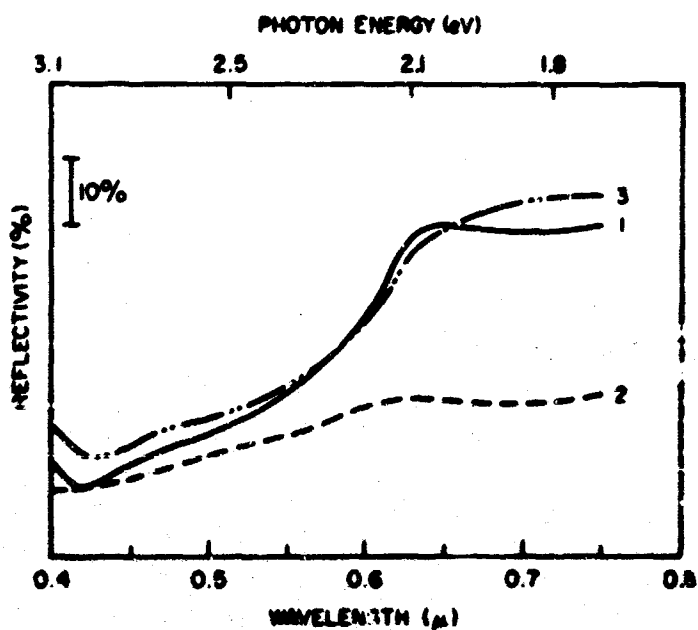


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# **LEAD OXIDE** **REFLECTIVITY COEFFICIENT (R)**



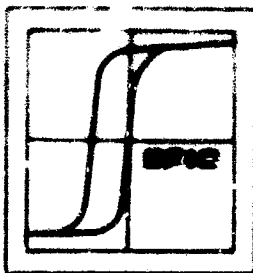
Reflection as a function of wavelength in a vacuum-deposited lead dioxide film.  
(Ref. 3281)



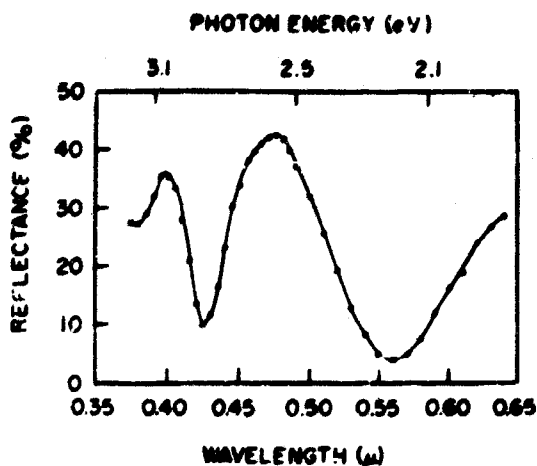
Reflection as a function of wavelength for red lead monoxide powder at 300°K.

1. Untreated sample
2. Defect points in the crystal are colored blue by an electric field ( $10^3$  V/cm)
3. Annealing at 300°C to destroy coloring.

(Ref. 14622)



**LEAD OXIDE  
REFLECTIVITY COEFFICIENT (R)**

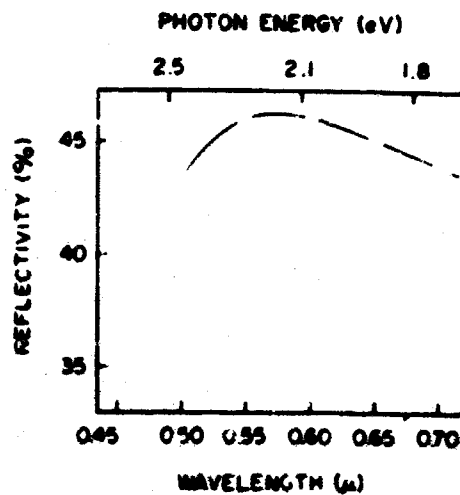


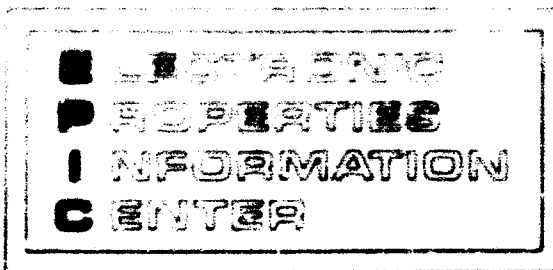
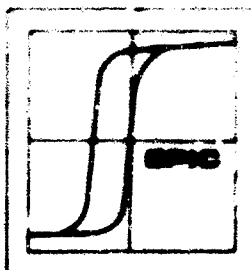
Reflectance of evaporated lead monoxide film .213 μ thick as a function of wavelength at 300°K.

(Ref. 4911)

Reflectivity of a 500 Å thick film of lead monoxide throughout the visible spectrum at 300°K.

(Ref. 11854)

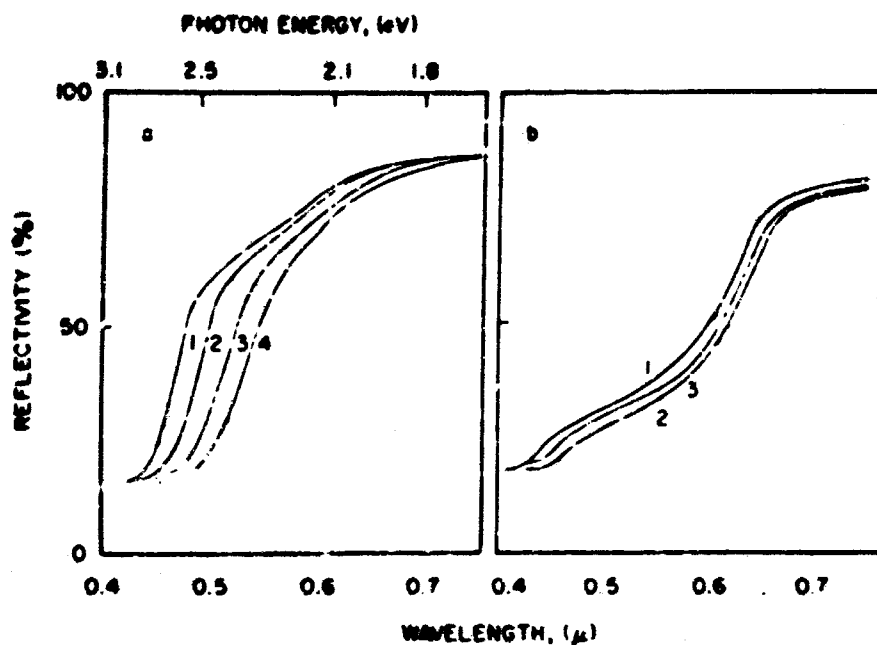




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## LEAD OXIDE

### REFLECTIVITY COEFFICIENT (R)



Reflectivity as a function of wavelength at various temperatures for two types of lead monoxide.

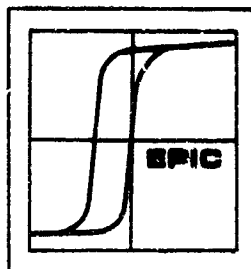
#### a Yellow lead oxide

1. 290°K
2. 354°K
3. 457°K
4. 537°K

#### b New annealed lead oxide

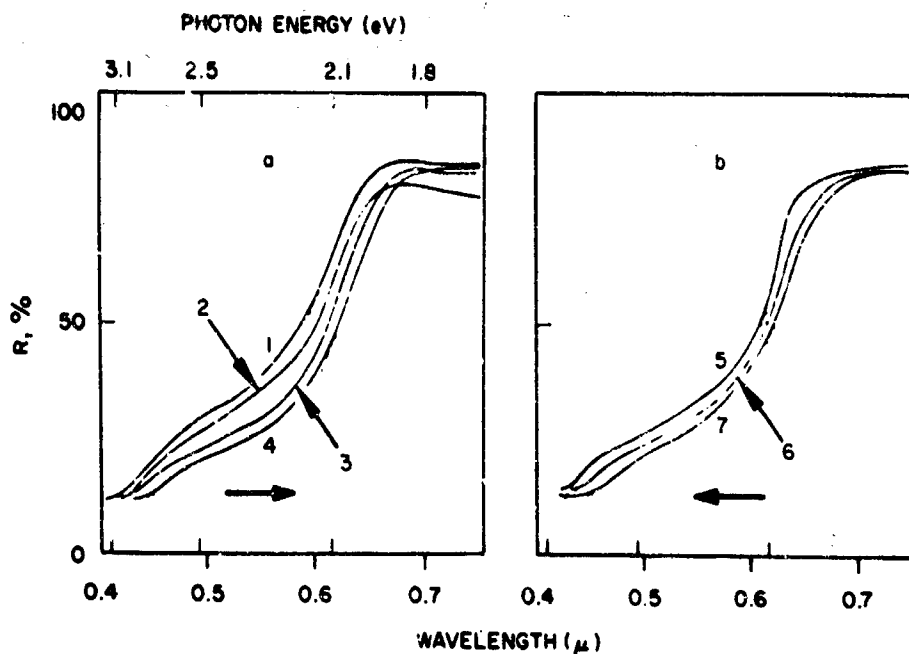
1. 290°K
2. 393°K
3. 573°K

(Ref. 14605)



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# LEAD OXIDE REFLECTIVITY COEFFICIENT (R)



Reflectivity as a function of wavelength in red, unannealed lead monoxide.

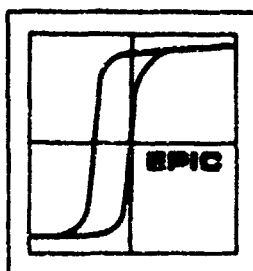
## a heating

1. 290°K
2. 342°K
3. 399°K
4. 573°K

## b cooling

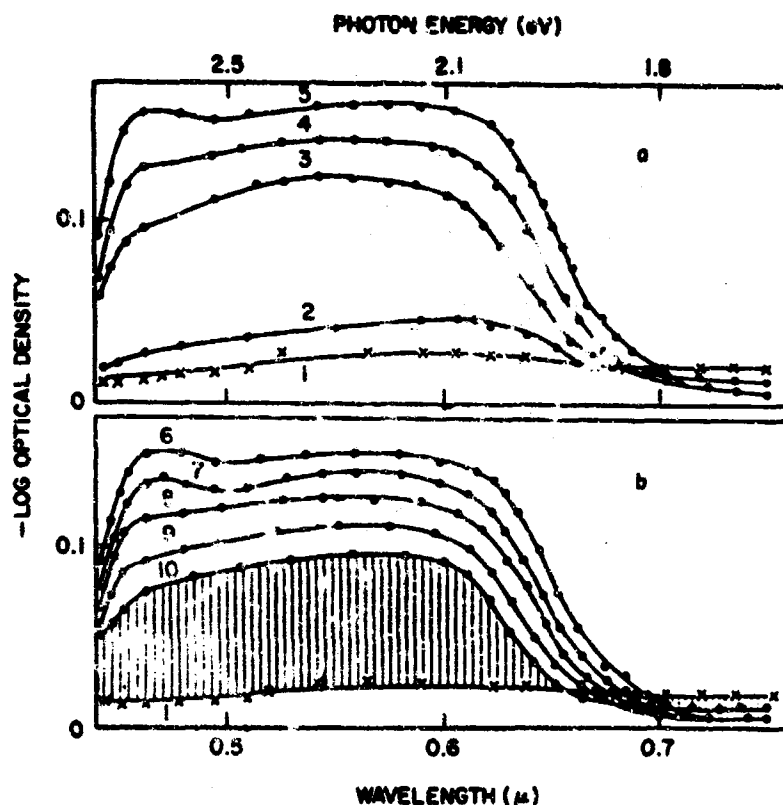
5. 290°K
6. 393°K
7. 573°K

After initial heating to 400°K, the energy gap and the reflectivity decrease irreversibly.  
(Ref. 14605)



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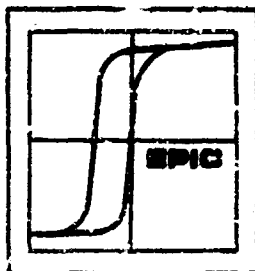
# LEAD OXIDE REFLECTIVITY COEFFICIENT (R)



Changes in the relative optical density of red unannealed PbO. Hatched area shows irreversible change in reflectivity in sample that has been heated to 573°K.

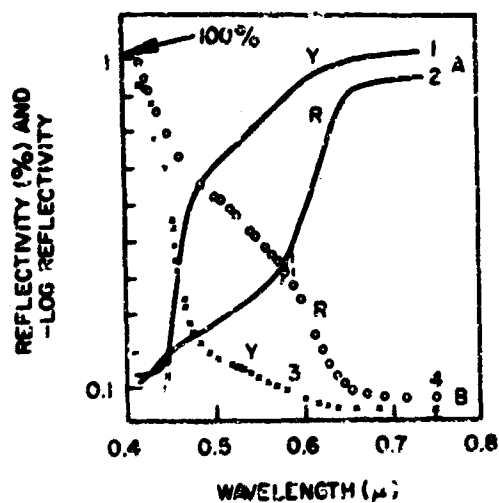
a heating	b cooling
1. Not-annealed	1. Not-annealed (base line for comparison)
2. 338°K	6. 498°K
3. 393°K	7. 438°K
4. 493°K	8. 373°K
5. 573°K	9. 333°K
	10. 293°K

(Ref. 14605)



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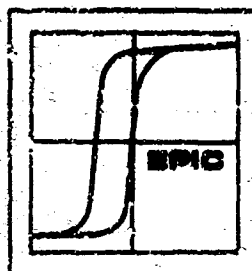
# LEAD OXIDE REFLECTIVITY COEFFICIENT (R)



1, 3 - yellow PbO films  
2, 4 - red PbO films

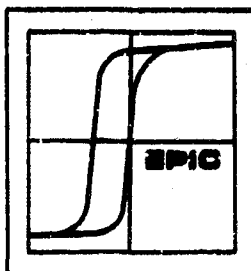
The reflectivity and the log reflectivity as a function of wavelength for both red and yellow lead monoxide films at 300°K. The values are taken relative to the reflectivity of magnesium oxide ( $PbO/MgO < 1$ , consequently the log of this ratio is negative). Curves A are reflectivity values, Curves B are the -log values.

(Ref. 14606)

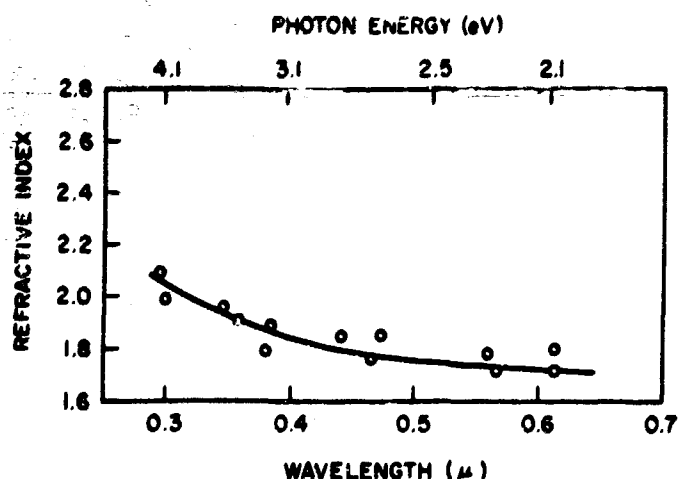


LEAD OXIDE  
REFRACTIVE INDEX (n)

Symbol	Value	Sample	Measurement Conditions		
			Wavelength	Temperature	Reference
$n_D$	~2.55	Yellow orthorhombic PbO films .213 $\mu$ , .235 $\mu$ and .25 $\mu$ thickness	$\lambda = 5896A$	300°K	4911
	2.75		$\lambda = 5200A$	300°K	4911
n	2.81		$\lambda = 5200A$ (green)	300°K	11854
	$\epsilon$ 2.535 $\frac{\omega}{\omega}$ 2.665	Litharge (red tetragonal)	$\lambda_{Li} = 6707A$	300°K	*
	2.51 2.71	Massicot (yellow orthorhombic)	$\lambda_{Li} = 6707A$	300°K	*
<u>Orien- tation</u>	<u>Value</u>				
x	2.51	Yellow orthorhombic PbO single crystal	$\lambda_{Li} = 6707A$	300°K	**
y	2.61				
z	2.71				
	2.42 $\pm$ 0.02	Pb <sub>3</sub> O <sub>4</sub> (Minimum) red	$\lambda_{Li} = 6707A$	300°K	**
*Larsen and Berman **Dana					



# LEAD OXIDE (n) REFRACTIVE INDEX

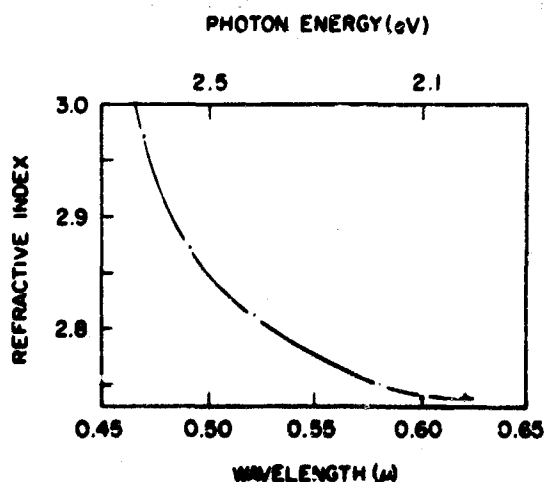


Refractive index as a function of wavelength in a lead dioxide polycrystalline film at 300°K.

(Ref. 3281)

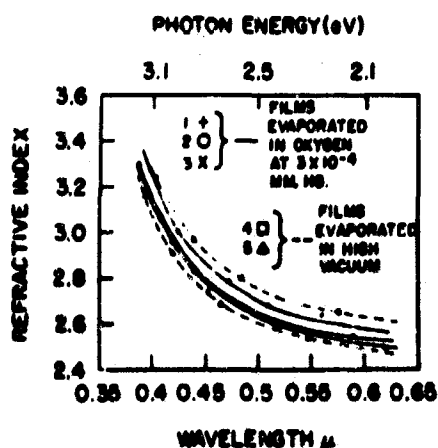
Refractive index as a function of wavelength in a lead monoxide film at 300°K. The film is highly reflecting, evaporated under oxygen pressure to prevent the presence of free lead.

(Ref. 11854)

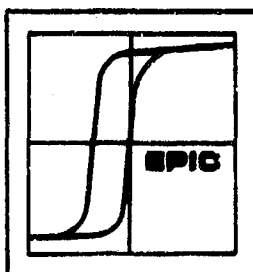


Refractive index as a function of wavelength for evaporated yellow orthorhombic lead monoxide films. The absorption is considerable when evaporated in a high vacuum, but can be greatly minimized when deposited at low oxygen pressure. This latter procedure apparently eliminates the free lead.

(Ref. 4911)







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# LEAD OXIDE

## THERMAL CONDUCTIVITY (k)

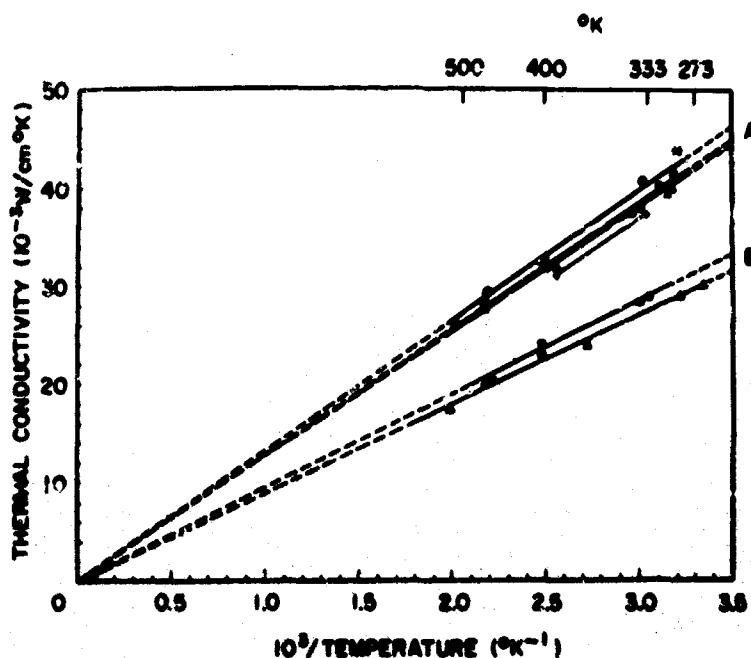
Value ( $10^{-2}$ W/cm $^{\circ}$ K)	Sample Yellow PbO single crystal platelets	Temperature	Reference
4.3	parallel to a-axis	298 $^{\circ}$ K	27776
3.1	parallel to b-axis	298 $^{\circ}$ K	27776
0.6	parallel to c-axis	298 $^{\circ}$ K	27776
Anisotropy of the thermal conductivity is believed to confirm theories regarding the binding energies in the three axis directions.			
2.77	PbO	311 $^{\circ}$ K	*
2.16	PbO	366 $^{\circ}$ K	*
1.71	PbO	422 $^{\circ}$ K	*

\*Handbook of Chem. and Phys., 47th Ed., 1966-1967. p. E-4.

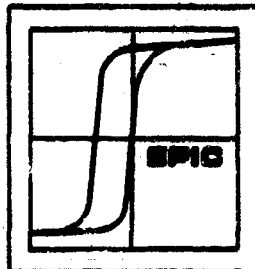
Thermal conductivity as a function of reciprocal temperature for yellow lead monoxide in single crystal platelets.

- A Parallel, to a-axis
- B Parallel, to b-axis

(Ref. 27776)



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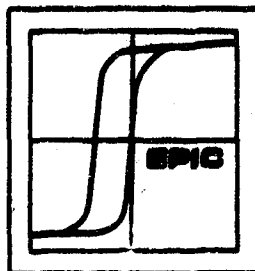
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**LEAD OXIDE  
THERMOELECTRIC PROPERTIES**

	Value (mV/°K)	Sample	Temperature	Reference
Thermal emf.	2 (max)	n-type, PbO <sub>2</sub>	~290°C	10517

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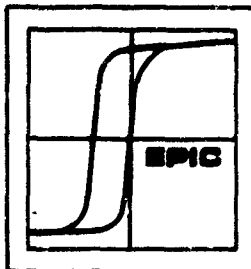


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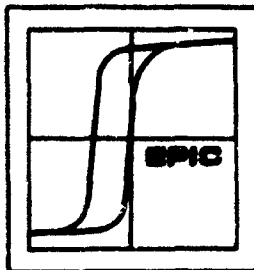
**LEAD OXIDE  
WORK FUNCTION**

Symbol	Value (eV)	Sample	Method	Temperature °K	Reference
$\phi$	>3	PbO film, annealed in oxygen at 400°C.	Secondary electron emission from 0 - 20 eV	300	21307

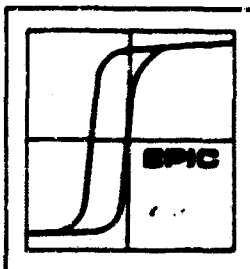


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DOCUMENT CONTROL DATA - R&D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author)  Hughes Aircraft Company Culver City, California 90232		2a. REPORT SECURITY CLASSIFICATION  Unclassified
		2b. GROUP
3. REPORT TITLE  Lead Oxide		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Data Sheets		
5. AUTHOR(S) (Last name, first name, initial)  Neuberger, M.		
6. REPORT DATE May 1967	7a. TOTAL NO. OF PAGES 70	7b. NO. OF REFS 37
8a. CONTRACT OR GRANT NO. AF 33(615)-2460	9a. ORIGINATOR'S REPORT NUMBER(S)  DS-155	
b. PROJECT NO. 7381		
c. No. 738103	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory (MAAM) Research and Technology Division Air Force Systems Command Wright-Patterson AFB, Ohio 45433	
13. ABSTRACT These data sheets present a compilation of a wide range of electronic properties for lead oxide. Electrical properties include conductivity, resistivity and dielectric constant. A wide variety of photoelectronic phenomena is shown. Energy data include energy bands, energy gap, and energy levels, as well as effective mass tables, phonon energy dispersion and work function. The optical properties include absorption, reflection, and refractive index. Data on several physical phenomena, such as thermal conductivity, Debye temperature, magnetic susceptibility and Richardson's Constant are presented. Thermo-electric data is given. Each property is compiled over the widest possible range of parameters including bulk and film form, from references obtained in a thorough literature search.  A summary of crystal structure and phase transitions has been included.		

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